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Novel ceramic substrates for high T_c superconductors

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Abstract. A group of complex perovskite oxides $REBa_2NbO_6$ (RE = La and Dy) have been synthesized and developed for their use as substrates for both $YBa_2Cu_3O_{7-\delta}$ and Bi(2223) superconductors. These materials have a complex cubic perovskite ($A_2BB'O_6$) structure with lattice constants, $a = 8{\cdot}48$–$8{\cdot}60$ Å. $REBa_2NbO_6$ did not show any phase transition in the temperature range 30–1300°C. The thermal expansion coefficient, thermal diffusivity and thermal conductivity values of $REBa_2NbO_6$ are favourable for their use as substrates for high T_c superconductors. The dielectric constant and loss factor of $REBa_2NbO_6$ are in a range suitable for their use as substrates for microwave applications. Both $YBa_2Cu_3O_{7-\delta}$ and Bi(2223) superconductors did not show any detectable chemical reaction with $REBa_2NbO_6$ even under extreme processing conditions. Dip coated $YBa_2Cu_3O_{7-\delta}$ thick films on polycrystalline $REBa_2NbO_6$ substrate gave a $T_c(0)$ of 92 K and a current density of $\sim 1{\cdot}1 \times 10^4$ A/cm^2 and Bi(2223) thick film on polycrystalline $REBa_2NbO_6$ substrate gave a $T_c(0)$ of 110 K and a current density of $\sim 4 \times 10^3$ A/cm^2 at 77 K and zero magnetic field. A laser ablated $YBa_2Cu_3O_{7-\delta}$ thin film deposited on polycrystalline $REBa_2NbO_6$ substrate gave a $T_c(0)$ of 90 K and a current density of $\sim 5 \times 10^5$ A/cm^2.

Keywords. High temperature superconductors; substrates; films.

1. Introduction

The discovery of superconductivity above liquid nitrogen temperature has evoked wide spread interest in producing these materials as thin films with high critical current density for various device applications (Wu *et al* 1989; Humphreys *et al* 1990; Wellstood *et al* 1994; Kurian *et al* 1998). Among the different copper oxide superconductors discovered so far, $YBa_2Cu_3O_{7-\delta}$ (YBCO) and $(Bi, Pb)_2Sr_2Ca_2Cu_3O_x$ [Bi(2223)] superconductors have gained considerable attention and a great deal of effort has been made for the production of high quality superconducting films of these compounds for suitable electronic applications. In the preparation of superconductor films, substrates play a vital role and the fundamental issues governing the role of the substrates in determining the properties of high T_c superconductor films developed on them have been highlighted in a recent review article (Phillips 1996). The chemical non reactivity between the substrate and the superconductor at the processing temperature is the most crucial factor for obtaining a high T_c superconductor film and the overriding importance of chemical compatibility over other substrate requirements in determining the suitability of a material as substrate for HTSC films has been emphasized in many recent articles (Koshy *et al* 1995; Phillips 1996). In addition, for microwave applications, the substrate should have low dielectric constant and loss factor. The conventional substrates such as Al_2O_3, Si, SiO_2, etc react with both YBCO and BSCCO superconductors at the processing temperature thereby reducing the transition temperature of the film drastically (Koshy *et al* 1994a, b, c, 1995; Phillips 1996). To the best of our knowledge MgO is the only conventional substrate suitable for both YBCO and Bi(2223) films for microwave applications. However, in the case of $YBa_2Cu_3O_{7-\delta}$, MgO forms an interlayer of barium salt at the YBCO–MgO interface if the processing temperature is above 700°C and reduces the superconducting transition temperature of the film drastically (Cheung and Ruekenstein 1989; Preng *et al* 1990). Also Bi(2223) films developed on MgO substrate always contained both the low T_c, Bi(2212) and high T_c, Bi(2223) phases (McGinnis and Briggs 1992; Agrawal *et al* 1993). In the course of our research work on the development of new substrate materials for high T_c superconductors, we have developed a new group of substrate materials, $REBa_2NbO_6$ (RE = La and Dy) which are found to be chemically non-reacting with both YBCO and Bi(2223) superconductors even under extreme processing conditions (Kurian *et al* 1996; Pai *et al* 1997a, b). $REBa_2NbO_6$ has moderately low dielectric constant and loss factor values making it suitable for microwave applications. $REBa_2NbO_6$ has a complex cubic perovskite structure and these materials did not show any phase transition in the temperature range 30–1300°C. The thermal expansion coefficient, thermal diffusivity

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and thermal conductivity values of $REBa_2NbO_6$ are in a range suitable for their use as substrates for YBCO and Bi(2223) superconductors. Dip-coated and melt textured YBCO and Bi(2223) thick films on polycrystalline $REBa_2NbO_6$ substrate gave $T_c(0)$ of 92 K and 110 K, respectively. Also the current densities of dip-coated YBCO and Bi(2223) thick films were ~ $1{\cdot}1 \times 10^4$ A/cm^2 and ~ 4×10^3 A/cm^2 at 77 K, respectively. A laser ablated YBCO thin film deposited on polycrystalline $REBa_2NbO_6$ substrate gave $T_c(0) = 90$ K and a current density of ~ 5×10^5 A/cm^2 at 77 K. In the present paper we describe the development of $REBa_2NbO_6$ as a substrate for both YBCO and Bi(2223) superconductors and the fabrication of superconducting YBCO and Bi(2223) films on these newly developed substrates.

2. Experimental

$REBa_2NbO_6$ (RE = La and Dy) were prepared following the conventional solid state reaction technique. High purity (99·9%) RE_2O_3, $BaCO_3$ and Nb_2O_5 were thoroughly wet mixed in the required stoichiometric ratio in an agate mortar with acetone as the wetting medium. The mixture was dried and calcined at 1100°C for 24 h in air with two intermediate grindings. The phase pure calcined powder was pelletized at a pressure of ~ 350 MPa in the form of circular discs having 13 mm diameter and ~ 2 mm thickness. These discs were sintered at 1400–1450°C for 12 h. The structure of these compounds was examined by the X-ray diffraction (XRD) technique using a computerized X-ray diffractometer (Rigaku Dmax/2C, Japan) with nickel filtered CuKα radiation. The differential thermal analysis (DTA) of $REBa_2NbO_6$ was carried out using Shimadzu DTA model 50 H (Japan) in the temperature range 30–1300°C. The specific heat capacity of $REBa_2NbO_6$ was determined from the differential scanning calorimetry (DSC) studies and the thermal diffusivity was measured by photo acoustic technique. Thermal expansion coefficient of $REBa_2NbO_6$ was measured using a Perkin Elmer Thermomechanical Analyser (TMA 7) with thermal analysis controller (TAC 7/DX). The dielectric constant (ε') and loss factor (tan δ) of polycrystalline $REBa_2NbO_6$ at liquid nitrogen temperature were studied using a Complex Impedance Analyser (HP 4192 A) in the frequency range 30 Hz–13 MHZ, with silver electrodes on both the sides of the sintered pellets. To examine the electrical and mechanical degradation of $REBa_2NbO_6$ under atmospheric conditions, humidity treatments were conducted by keeping the sintered $REBa_2NbO_6$ samples in boiling water for 2 h. The electrical resistivity and density of the humidity treated $REBa_2NbO_6$ samples were measured after drying.

The chemical reactivity between $REBa_2NbO_6$ and YBCO was studied by mixing $REBa_2NbO_6$ and YBCO in 1 : 1 volume ratio and the composite mixture was pressed in the form of circular discs of 10 mm diameter and ~ 1·5 mm thickness. These discs were annealed at 950°C for 15 h in air followed by slow cooling. The YBCO powder used for the study has been prepared from high purity Y_2O_3, $BaCO_3$ and CuO by solid state reaction. The chemical reactivity between $REBa_2NbO_6$ and YBCO was studied by XRD. Single phase Bi(2223) powder used in the present study was prepared by the conventional solid state reaction method and details of the preparation are given in one of our earlier publications (Koshy *et al* 1994a). The chemical reactivity between $REBa_2NbO_6$ and Bi(2223) was studied by thoroughly mixing 1 : 1 volume ratio of Bi(2223) and $REBa_2NbO_6$ and the composite mixture was pressed in the form of circular discs with dimensions of 10 mm diameter and ~ 1·5 mm thickness by applying a pressure of ~ 300 MPa. These circular discs were then annealed in air at 850°C for 10 h and slow cooled at a rate of 1°C/min up to 800°C and then furnace cooled to room temperature. The chemical reactivity of $REBa_2NbO_6$ with Bi(2223) was studied up to a temperature of 850°C by powder X-ray diffraction technique.

The YBCO and Bi(2223) suspension for dip-coating were prepared by mixing YBCO and Bi(2223) powders with isopropyl alcohol or *n*-butanol and the viscosity of the suspension was controlled by the addition of commercially available fish oil. The polished and cleaned $REBa_2NbO_6$ substrate was then dipped in the respective suspension and dried. This step is repeated till a required thickness is attained. The dip-coated YBCO films were then dried in an oven and heated in a programmable furnace at a rate of 5°C/min in air up to 1000°C and kept at this temperature for 2 min. The films were then cooled at the rate of 2°C/min up to 940°C and annealed at this temperature for 60 min. The films were cooled to room temperature at a rate of 1°C/min. The dip coated Bi(2223) films were dried in an oven and heated in a programmable furnace at a rate of 5°C/min in air up to 880°C and kept at this temperature for 2 min and then annealed at 850°C temperature for 6 h. The films were cooled at a rate of 1°C/min up to 800°C from the annealing temperature of 850°C and then furnace cooled to room temperature. The structure of the dip-coated YBCO and Bi(2223) thick films was examined by X-ray diffraction. The superconductivity of these films was studied by temperature-resistance measurements using the four-probe technique. A Keithley current source model 221 and Keithley nanovoltmeter model 181 were used for resistance measurements. The temperature of the samples was measured by a calibrated copper-constantan thermocouple with an accuracy of $\pm$ 0·2 K. The critical current density of the superconducting YBCO and Bi(2223) films was measured on thick films coated on rectangular (10 mm × 2 mm) substrates by standard four-probe method using the 1 μV/cm criterion.

Laser ablation experiments were carried out using a Lamda Physik 301 KrF 248 nm excimer laser and 300 mm focal length quartz lens for laser beam focussing. The excimer laser pulse had a maximum energy of 1200 mJ with a pulse width of 25 ns and a 1–10 Hz variable repetition rate. The experimental details for the *in situ* growth of YBCO films are given in an earlier paper (Pinto *et al* 1992). In the present experiment, the YBCO films were grown on polycrystalline $REBa_2NbO_6$ substrates at a substrate temperature of 800°C and the energy density of the laser beam was 2·2 J/cm^2. The YBCO film had a thickness of 4000 Å. The structure of the laser ablated YBCO thin film was examined by XRD and the superconductivity by temperature-resistance measurements.

3. Results and discussion

The powder X-ray diffraction patterns of sintered $REBa_2NbO_6$ samples are shown in figure 1. The XRD patterns clearly show that these materials are isostructural with other cubic perovskites with the general formula $A_2(BB')O_6$, such as $ErBa_2SbO_6$, YBa_2NbO_6, $DyBa_2SbO_6$ etc reported in the JCPDS file in which doubling of the basic perovskite unit cell is observed. Doubling of the perovskite unit cell in $REBa_2NbO_6$ is due to the ordering of RE and Nb atoms on the octahedral sites (Zhang and Wang 1991). Presence of superstructural lines in the XRD pattern shown in figure 1 indicates the ordering of the basic ABO_3 perovskite unit cell in $REBa_2NbO_6$ material. The DTA analysis of $REBa_2NbO_6$ showed that there is no phase transition up to a temperature of 1300°C. The various physical properties of the $REBa_2NbO_6$ materials are summarized in table 1. The thermal conductivity (K) of $REBa_2NbO_6$ was calculated from the experimentally observed values of thermal diffusivity (α) and specific heat capacity (c) using the relation

$$K = \alpha \rho c,$$

where ρ is the density of the material. Detailed studies on the thermal properties of $REBa_2NbO_6$ will be reported elsewhere. The higher thermal conductivity of $REBa_2NbO_6$ as compared to the thermal conductivity of conventionally used substrate materials such as Al_2O_3, MgO etc is an added advantage for substrate applications. The sintered density of $REBa_2NbO_6$ measured by Archimedes method is ~97% of the calculated theoretical density and the room temperature resistivity of $REBa_2NbO_6$ was ~ 10^{10} Ωcm. The electrical resistivity and density of the humidity treated $REBa_2NbO_6$ samples, measured after drying, were same as that of the sintered samples indicating that $REBa_2NbO_6$ is highly stable under atmosphere conditions. The sintered samples were mechanically strong and could be sliced into thin pieces of 0·5 mm thickness by a diamond cutter. Good reflecting surfaces were obtained by mechanical polishing. Organic solvents such as alcohol, carbon tetrachloride, trichloroethylene etc could be used as effective cleaning agents. The XRD pattern of melted and subsequently quenched $REBa_2NbO_6$ sample was identical to that of sintered $REBa_2NbO_6$ sample, indicating that this material melts congruently and could be grown as single crystals from the melt.

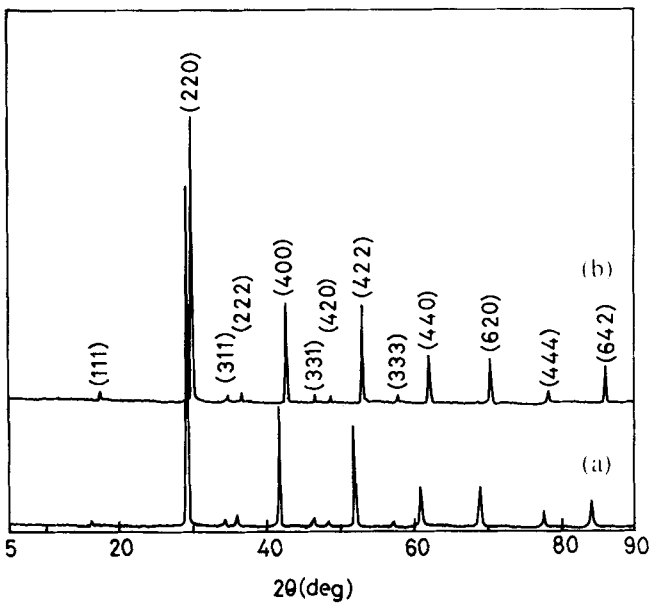

Figure 1. Powder X-ray diffraction pattern of sintered (a) $LaBa_2NbO_6$ and (b) $DyBa_2NbO_6$.

The variation of dielectric constant (ε') and loss factor ($\tan\delta$) at 77 K with frequency are shown in figures 2 and 3 respectively. The loss factor values for $REBa_2NbO_6$ samples measured at liquid nitrogen temperature were found to be lower than the values reported at room temperature. However, no substantial change was observed for dielectric constant at liquid nitrogen temperature and room temperature. The values of ε' and $\tan\delta$ are comparable to those of $LaAlO_3$ and are in a range suitable for their use as substrates for microwave applications.

One of the most important criteria for the selection of any material as a substrate for YBCO and Bi(2223) superconductors is the chemical non-reactivity between the substrate and the film at the processing temperature. In order to see whether $REBa_2NbO_6$ is chemically compatible with YBCO, the chemical reactivity of $REBa_2NbO_6$ with YBCO was studied at temperatures up to 950°C. Superconducting YBCO powder was mixed with $REBa_2NbO_6$ in a 1 : 1 volume ratio and pressed in the form of pellets which were then annealed at 950°C for 15 h and cooled slowly to room temperature. The XRD patterns of annealed samples of 1 : 1 volume mixture of YBCO and $REBa_2NbO_6$ are shown in figure 4. X-ray

Table 1. Physical properties of $REBa_2NbO_6$ measured at room temperature.

Substrate properties	$LaBa_2NbO_6$	$DyBa_2NbO_6$
Crystal structure	Cubic, $a = 8{\cdot}6$ Å	Cubic, $a = 8{\cdot}48$ Å
Dielectric constant (ε') at 10 MHz	29	29
Dielectric loss ($\tan\delta$) at 10 MHz, at 77 K	4×10^{-4}	3×10^{-4}
Thermal expansion coefficient ($°C^{-1}$)	$7{\cdot}71 \times 10^{-6}$	$7{\cdot}806 \times 10^{-6}$
Thermal conductivity ($Wm^{-1}K^{-1}$)	81	68
Specific heat capacity ($JKg^{-1}K^{-1}$)	590	430
Resistivity (Ωcm)	$\sim 10^{10}$	$\sim 10^{10}$

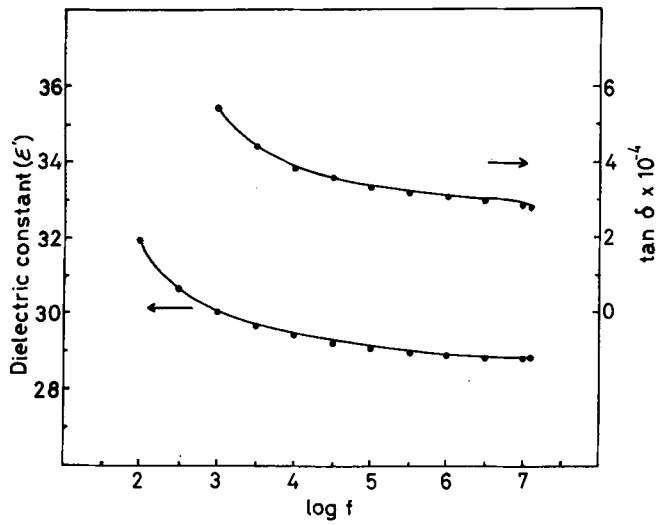

Figure 2. Variation of dielectric constant (ε') and loss factor ($\tan\delta$) of $LaBa_2NbO_6$ with frequency at liquid nitrogen temperature.

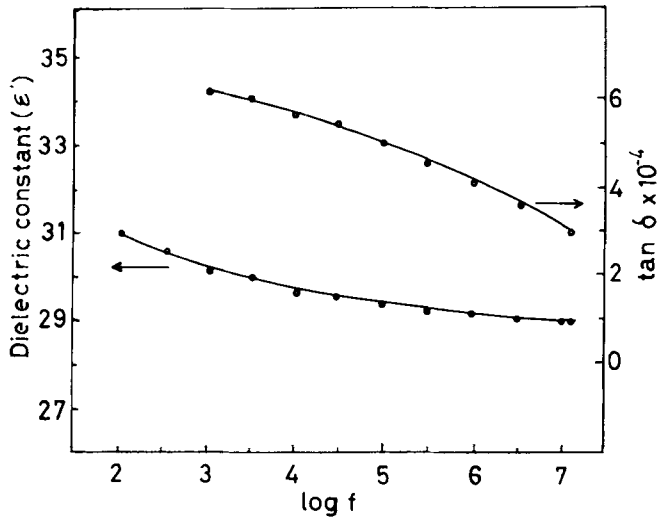

Figure 3. Variation of dielectric constant (ε') and loss factor ($\tan\delta$) of $DyBa_2NbO_6$ with frequency at liquid nitrogen temperature.

diffraction patterns of the two phases in the annealed samples (figures 4b–c) were compared with those of pure YBCO (figure 4a) and pure $REBa_2NbO_6$ (figure 1). It is clear from these figures (4b–c) that there was no new additional phase formed (within the precision of powder XRD technique) besides YBCO and $REBa_2NbO_6$ in the YBCO–$REBa_2NbO_6$ composites. Similarly, the chemical reactivity of $REBa_2NbO_6$ with Bi(2223) was studied by 1 : 1 volume ratio of Bi(2223) and $REBa_2NbO_6$ and annealing the pressed pellet at 850°C for 15 h. The XRD patterns of annealed samples of 1 : 1 volume mixture of $REBa_2NbO_6$ and Bi(2223) are shown in figure 5. The XRD pattern of the two phases (figure 5c) in the annealed Bi(2223)–$DyBa_2NbO_6$ sample as typical example, is compared with those of pure Bi(2223) (figure 5a) and $DyBa_2NbO_6$ (figure 5b). It is clear from figure 5 that there is no additional phase formed, not even Bi(2212), within the precision of XRD technique, other than Bi(2223) and $REBa_2NbO_6$ in the composite. These results indicate that $REBa_2NbO_6$ is chemically compatible with both YBCO and Bi(2223) superconductors.

The suitability of $REBa_2NbO_6$ as a substrate for YBCO and Bi(2223) superconductors was confirmed by dip-coating thick films of YBCO and Bi(2223) on polycrystalline $REBa_2NbO_6$ substrates. Figures 6 and 7 show the XRD pattern of YBCO and Bi(2223) thick films dip-coated on $DyBa_2NbO_6$, respectively, as a typical example. In figure 6 all the peaks except that of the characteristic peaks of $DyBa_2NbO_6$ are due to orthorhombic YBCO phase. The XRD pattern of Bi(2223) thick films on $DyBa_2NbO_6$ (figure 7) shows that except for the characteristic peaks of $DyBa_2NbO_6$, all other peaks are those of Bi(2223) superconductor. Figures 8 and 9 show the temperature vs resistance curve of YBCO and Bi(2223) thick film developed on polycrystalline $DyBa_2NbO_6$ substrate, respectively. The film showed metallic behaviour in the normal state and gave a zero resistance transition at 92 K for YBCO and 110 K for Bi(2223) thick films on $DyBa_2NbO_6$ with a superconducting transition width of ~ 1·5 K. The critical current density of YBCO and Bi(2223) thick film on $DyBa_2NbO_6$ was measured at 77 K using 1 μV/cm criterion under

zero applied magnetic field which was found to be ~ $1{\cdot}1 \times 10^4$ A/cm^2 and ~ 4×10^3 A/cm^2, respectively. The high transition temperatures obtained in superconducting YBCO and Bi(2223) with $DyBa_2NbO_6$ can be attributed to the chemical nonreactivity of YBCO and Bi(2223) with $DyBa_2NbO_6$ substrate even at the processing temperature. The dip-coated YBCO and Bi(2223) thick films had excellent adhesion with the $DyBa_2NbO_6$ substrate and the film thickness was 4 μm.

Figure 10 shows the XRD pattern of YBCO thin film developed on polycrystalline $LaBa_2NbO_6$ substrate by pulsed laser ablation. In the XRD pattern all the peaks except that of characteristic peaks of $LaBa_2NbO_6$ are due to the orthorhombic YBCO phase. Also a high degree of c-axis orientation is evident from the XRD pattern of the film. The peaks corresponding to (00*l*) orientation of YBCO are as sharp and intense as those

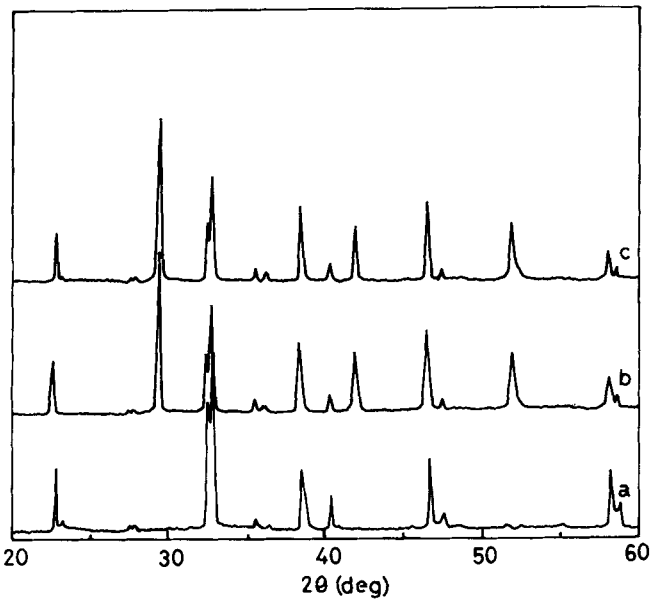

Figure 4. Powder X-ray diffraction pattern of (a) phase pure YBCO, (b) 1 : 1 volume mixture of YBCO and $LaBa_2NbO_6$ annealed at 950°C for 15 h and (c) 1 : 1 volume mixture of YBCO and $DyBa_2NbO_6$ annealed at 950°C for 15 h.

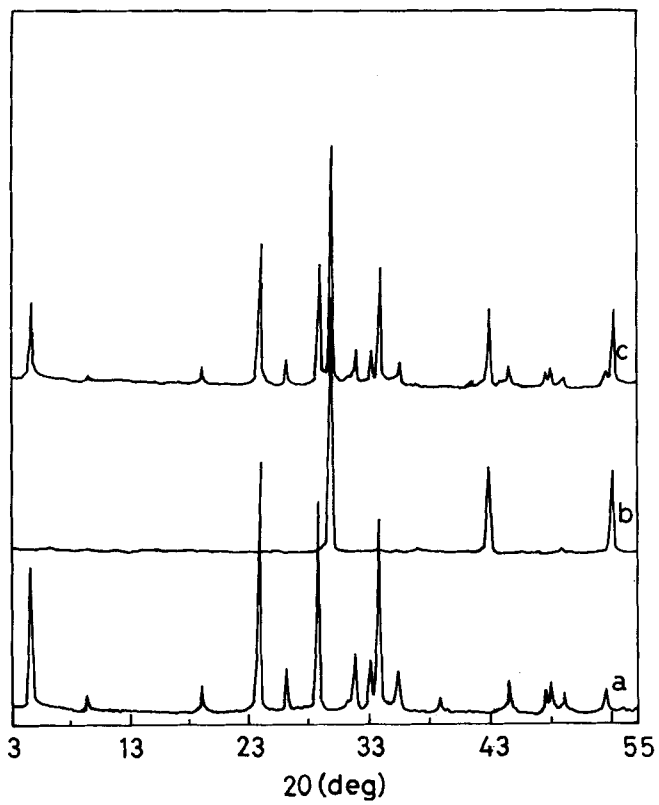

Figure 5. Powder X-ray diffraction pattern of (a) phase pure Bi(2223) superconductor, (b) phase pure $DyBa_2NbO_6$ and (c) 1 : 1 volume mixture of Bi(2223) and $DyBa_2NbO_6$ annealed at 850°C for 10 h.

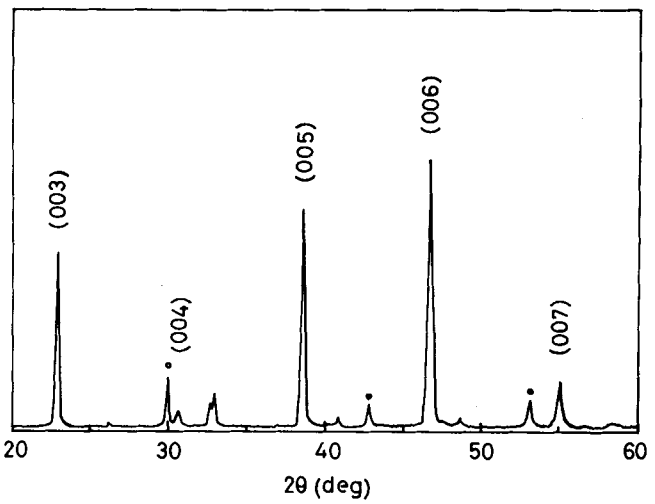

Figure 6. X-ray diffraction pattern of dip-coated $YBa_2Cu_3O_{7-\delta}$ thick film on $DyBa_2NbO_6$ substrate. (Substrate peaks are marked by 'o').

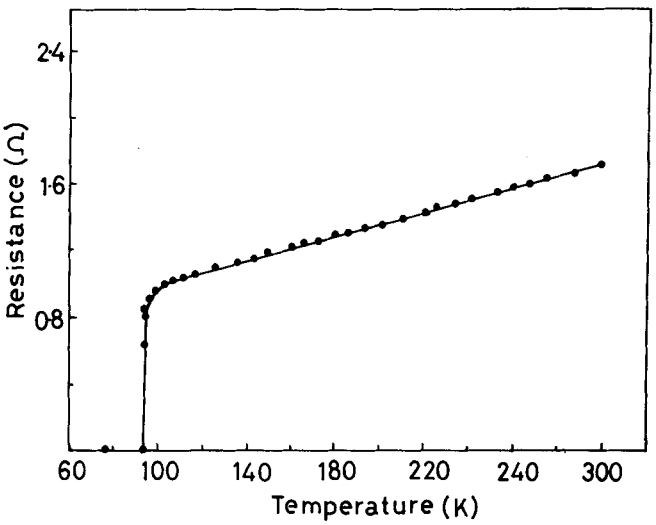

Figure 7. X-ray diffraction pattern of dip-coated Bi(2223) thick film on $DyBa_2NbO_6$ substrate. (Substrate peaks are marked by '•').

of YBCO films on $LaAlO_3$ (001) substrate indicating good crystallinity of the grains of the YBCO film. The temperature-resistance curve for the YBCO thin film on polycrystalline $LaBa_2NbO_6$ is shown in figure 11. The film showed metallic behaviour in the normal state and gave $T_c(0)$ of 90 K and J_c of 5×10^5 A/cm^2 at 77 K in zero magnetic field.

4. Conclusion

A group of novel substrate materials, $REBa_2NbO_6$ have been synthesized and developed for their use as substrates for YBCO and Bi(2223) superconductors. These materials have a complex cubic perovskite structure $[A_2(BB')O_6]$ with lattice constants, $a = 8{\cdot}48$–$8{\cdot}60$ Å. $REBa_2NbO_6$ did not show any phase transition in the temperature range 30–1300°C. The thermal expansion coefficient values, thermal diffusivity and thermal conductivity values of $REBa_2NbO_6$ are favourable for their use as substrates for high T_c superconductors. The dielectric constant and loss factor values of sintered $REBa_2NbO_6$ are in a range suitable for its use as substrate for microwave applications. It was found that $REBa_2NbO_6$ did not react with YBCO and Bi(2223) even under severe heat treatment conditions. Superconducting YBCO and Bi(2223) thick films prepared by dip-coating on polycrystalline $DyBa_2NbO_6$ gave $T_c(0)$ of 92 K and 110 K, respectively.

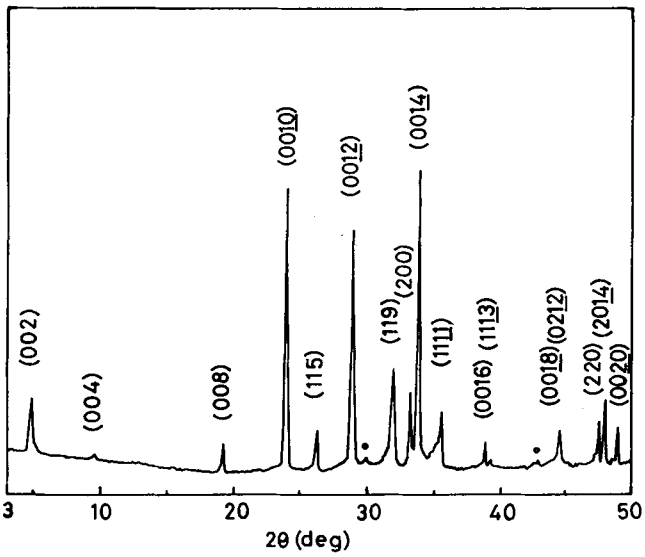

Figure 8. Temperature-resistance curve of dip-coated $YBa_2Cu_3O_{7-\delta}$ thick film on $DyBa_2NbO_6$ substrate.

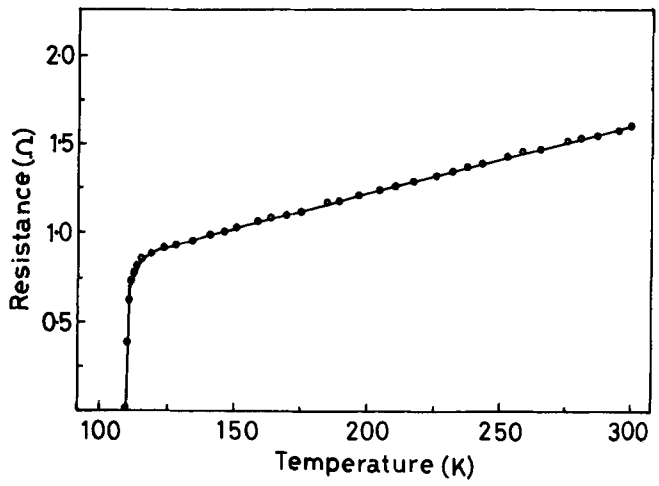

Figure 9. Temperature-resistance curve of dip-coated Bi(2223) thick film on $DyBa_2NbO_6$ substrate.

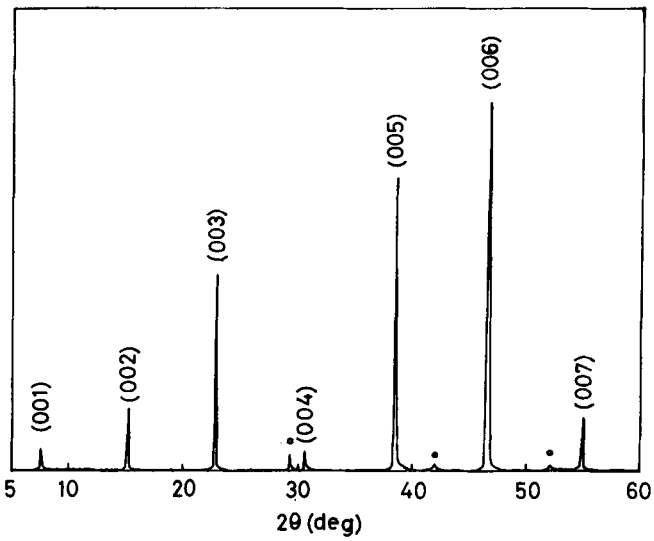

Figure 10. X-ray diffraction pattern of laser ablated $YBa_2Cu_3O_{7-\delta}$ thin film on $LaBa_2NbO_6$ substrate. (Substrate peaks are marked by 'o').

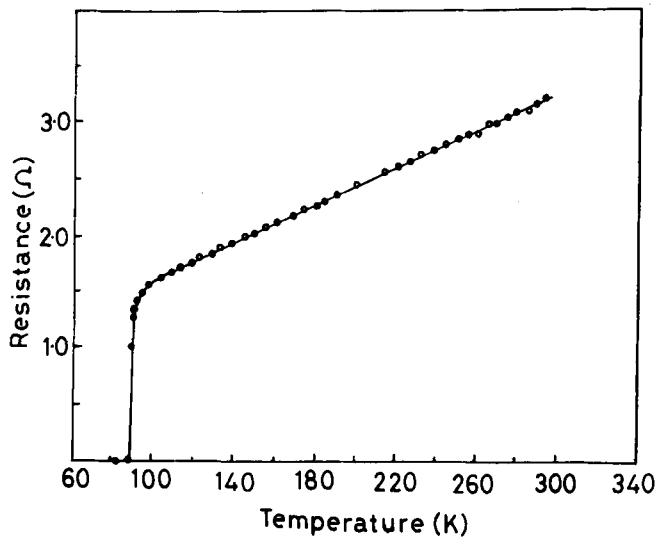

Figure 11. Temperature-resistance curve of laser ablated $YBa_2Cu_3O_{7-\delta}$ thin film on $LaBa_2NbO_6$ substrate.

The critical current density of YBCO and Bi(2223) thick film on $DyBa_2NbO_6$ was measured at 77 K using 1 μV/cm criterion under zero applied magnetic field which was found to be $\sim 1{\cdot}1 \times 10^4$ A/cm^2 and $\sim 4 \times 10^3$ A/cm^2, respectively. Superconducting YBCO thin films developed on $LaBa_2NbO_6$ substrate gave a $T_c(0) = 90$ K and critical current density 5×10^5 A/cm^2 at 77 K.

Acknowledgement

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References

Agrawal A, Gupta R P, Khokale W S, Kundra K D, Deshmukh P R, Singh M and Vyas P D 1993 *Supercond. Sci. Technol.* **6** 670

Cheung C T and Ruekenstein E 1989 *J. Mater. Res.* **4** 1

Humphreys R G, Satchell J S, Chew N G, Edwards J A, Goodyear S W, Blenkinsop S E, Dosser O D and Cullis A G 1990 *Supercond. Sci. Technol.* **3** 38

Koshy J, Kumar K S, Yadava Y P and Damodaran A D 1994a *J. Mater. Sci. Lett.* **13** 670

Koshy J, Kumar K S, Kurian J, Yadava Y P and Damodaran A D 1994b *Physica C* **234** 211

Koshy J, Kurian J, Thomas J K, Yadava Y P and Damodaran A D 1994c *Jpn. J. Appl. Phys.* **33** 117

Koshy J, Kumar K S, Kurian J, Yadava Y P and Damodaran A D 1995 *J. Am. Ceram. Soc.* **78** 3088

Kurian J, Varma H K, Koshy J, Pai S P and Pinto R 1996 *Appl. Phys. Lett.* **69** 2909

Kurian J, Asha M John, Sajith P K, Koshy J, Pai S P, Pinto R 1998 *Jpn. J. Appl. Phys.* **37** L1144

Mc Ginnis W C and Briggs J J 1992 *J. Mater. Res.* **7** 585

Pai S P, Jesudasan J, Apte P R, Pinto R, Kurian J, Sajith P K, James J and Koshy J 1997a *Europhys. Lett.* **39** 669

Pai S P, Jesudasan J, Apte P R, Pinto R, Kurian J, Sajith P K, James J and Koshy J 1997b *Physica C* **290** 105

Phillips J M 1996 *J. Appl. Phys.* **79** 1829

Pinto R, Pai S P, D' Souza C P, Gupta L C, Vijayaraghavan R, Kumar D and Sharon M 1992 *Physica C* **196** 264

Preng L H, Chin T S, Chen K C and Lin C H 1990 *Supercond. Sci. Technol.* **3** 233

Wellstood F C, Kingstone J J and Clarke J 1994 *J. Appl. Phys.* **75** 683

Wu X D, Dutta B, Hegde M S, Inam A, Venkitasan T, Chase E W, Chang C C and Howard R 1989 *Appl. Phys. Lett.* **54** 179

Zhang X and Wang Q 1991 *J. Am. Ceram. Soc.* **74** 2846