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Ba_2RETaO_6 (*RE* = Pr, Nd, Eu, and Dy), A Group of Chemically Stable Substrates for $YBa_2Cu_3O_{7-\delta}$ Films

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A group of complex perovskites, Ba_2RETaO_6 (where *RE* = Pr, Nd, Eu, and Dy) has been synthesised and sintered as single phase materials with high sintered density and stability by solid state reaction. All compounds were found to be isostructural, having a complex cubic perovskite crystal structure of the general formula $A_2(BB')O_6$ with the lattice constant value in the range from 8.55 to 8.44 Å. The values of the dielectric constant and the loss factor for these materials are in the range suitable for the use as substrates for microwave applications of superconductor films. The $YBa_2Cu_3O_{7-\delta}$ superconductor showed no chemical reaction with Ba_2RETaO_6 ceramics even when they were mixed in composites of the form 80 vol% YBCO–20 vol% Ba_2RETaO_6 and processed in air up to 1223 K. All the composites showed a $T_{c(0)}$ of 92 K. The YBCO thick films fabricated on polycrystalline Ba_2RETaO_6 specimens by dip coating and partial melting techniques showed (00*l*) orientation with $T_{c(0)}$ of 92 K. © 1996 Academic Press, Inc.

1. INTRODUCTION

Exploration of new ceramics as substrates for $YBa_2Cu_3O_{7-\delta}$ superconductor films remains to be an exciting area of research (1–4). The substrate plays an important role in the development of good quality superconducting films with high critical current density. Many compounds such as $SrTiO_3$, MgO, and $LaAlO_3$ are in use as substrates for $YBa_2Cu_3O_{7-\delta}$ (YBCO) films (5–8). Even MgO, the most widely used substrate for YBCO superconductors does form an interlayer of Ba salt at the YBCO–MgO interface if the processing temperature is above 973 K and reduces the superconducting transition temperature of YBCO considerably (9, 10). Recently, some polycrystalline ceramics, such as $Ba_2DySnO_{5.5}$ (11) and Ba_2GdNbO_6 (12), were reported to possess excellent qualities of an ideal substrate for $YBa_2Cu_3O_{7-\delta}$ films. In our search for new materials as suitable substrates for YBCO films, we have now developed a group of complex cubic perovskites, Ba_2RETaO_6 (where *RE* = Pr, Nd, Eu, and Dy) which are found to be chemically nonreactive with YBCO superconductors under severe heat treatment and have moderately low dielectric constant and loss factor. Here, we report the synthesis, characterization, and sintering of Ba_2RETaO_6 ceramics and their suitability as potential substrates for YBCO superconductor films.

2. EXPERIMENTAL

The polycrystalline Ba_2RETaO_6 (where *RE* = Pr, Nd, Eu, and Dy) compounds were synthesized by mixing stoichiometric amounts of high purity (99.9%) rare earth oxides, $BaCO_3$ and Ta_2O_5, followed by calcination of pressed pellets at 1373–1423 K for 50 h with three intermediate grindings. The calcined materials, after a thorough grinding, were pressed uniaxially at a pressure of 5 ton/cm^2 in the form of disks with dimensions 13 mm in diameter and 1–3 mm in thickness. Pressed pellets were sintered in air at temperatures of 1623–1673 K for 24 h and furnace cooled slowly. Bulk density of the sintered specimens was determined by the Archimedes method.

Phase purity of the samples was checked by powder X-ray diffraction method (XRD) using a Rigaku X-ray diffractometer with nickel filtered Cu$K\alpha$ radiation. Differential thermal analysis of sintered specimens was carried out to examine whether these compounds undergo phase transitions in the temperatures 300–1373 K using the Sieko TG/DTA Instrument (Model SSC/5200H, Sieko Instruments Inc., Japan). The stability and degradation of Ba_2RETaO_6 compounds were investigated by electrical resistivity and density measurements. For this, humidity treatment was carried out by keeping the sintered specimens in boiling water for few hours. Density and electrical resistivity of these materials were determined before and after humidity treatment. The electrical resistivity measurements were done by the standard four probe method using a Keithley current source (Model 220), a Keithley nanovoltmeter (Model 181), and a calibrated copper constantan thermocouple with an accuracy of ±1 K. A complex impedance analyzer (HP 4192 A) was used for determination of dielectric constant and loss factor values in the frequency range from 30 Hz to 13 MHz at 77 and 300 K with silver

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electrodes on both sides of a circular disk. Melting experiments were also carried out on Ba_2RETaO_6 powder in a platinum crucible. These compounds were found to melt at ~2120 K. Thus melted samples were quenched in air and their phase purity was examined by XRD technique.

For the chemical reactivity studies, the composites of Ba_2RETaO_6 and YBCO (prepared from high purity Y_2O_3, $BaCo_3$, and CuO by solid state reaction) were prepared in 20 vol%–80 vol% ratio, respectively, and pressed pellets of the composites were heat treated up to 1223 K for 20 h in air and annealed at 733 K for 30 h under flowing oxygen. The chemical reactivity was studied by powder XRD and electrical resistivity measurement. Sintered and highly polished Ba_2RETaO_6 specimens were used for the fabrication of YBCO thick films by dip coating and partial melting techniques. Presintered YBCO powder was deposited on polished substrates by dipping the polished substrate (smooth side only) into a YBCO suspension made by thorough grinding of YBCO powder in *n*-butanol and drying. This process was continued up to the required film thickness. Finally, deposited films were dried in oven at 373 K. The thickness of the films was <5 μm. The YBCO thick films were heat treated in a program able tube furnace at a heating rate of 5 K/min to 1293 K, soaked for 2–5 min, cooled at 5 K/min to 1223 K, and soaked for 2–4 h. Then the thick films were cooled slowly to 733 K and annealed at that temperature for 30 h under flowing oxygen. Heat treatment of the films up to 1293 K caused partial melting of the YBCO film, which facilitates good adhesion of the film to the substrate. The structure of the YBCO thick films was studied by XRD and the superconducting transition temperature was determined by temperature vs resistance measurement.

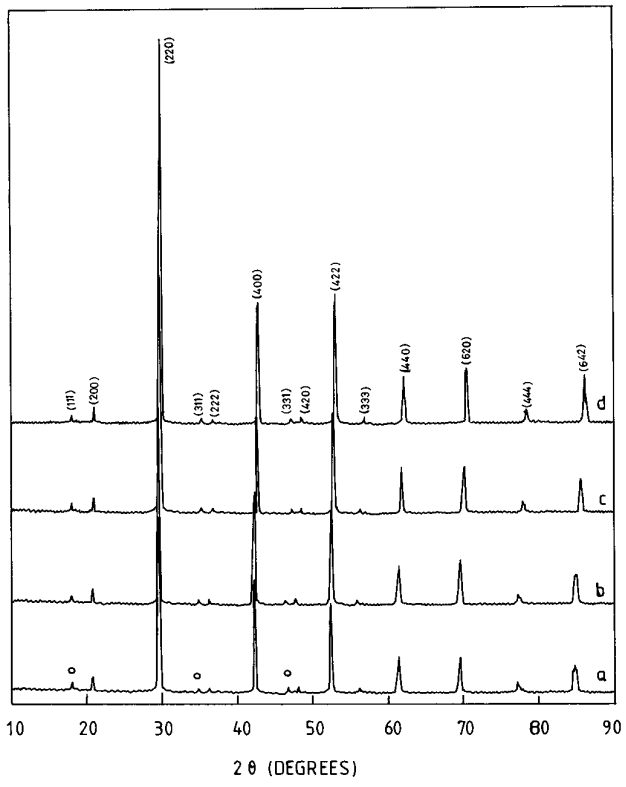

FIG. 1. X-ray diffraction patterns of sintered (a) Ba_2PrTaO_6, (b) Ba_2NdTaO_6, (c) Ba_2EuTaO_6, and (d) Ba_2DyTaO_6 compounds. The superstructure lines are marked by 'o'.

3. RESULTS AND DISCUSSION

Figure 1 shows the powder XRD patterns recorded at room temperature for the sintered Ba_2RETaO_6 (where RE = Pr, Nd, Eu, and Dy) ceramics and the XRD data are given in Table 1. It was observed that the XRD patterns were similar, indicating that these compounds were isostructural. However, the peak positions steadily shifted to higher 2θ values as Pr was successively replaced by relatively smaller rare earth ions. The Ba_2RETaO_6 compounds were also found to be isostructural with other rare earth cubic perovskites of the general formula $A_2(BB')O_6$ (13, 14), such as Ba_2EuNbO_6, Ba_2ErSbO_6, and Ba_2YNbO_6 reported in JCPDS files, in which doubling of the basic perovskite unit cell was observed. The doubling of the basic perovskite unit cell in the Ba_2RETaO_6 ceramics was due to the ordering of RE^{3+} ions and Ta^{5+} ions at the octrahedral sites, resulting in a superstructure of perovskite unit cell. This was seen by the presence of superstructural lines in the XRD pattern (Fig. 1). The lattice parameter a, determined from simple least squares refinements using all XRD peak positions for 2θ values from 10° to 90°, steadily decreased and was in the range from 8.55 Å for Ba_2PrTaO_6 to 8.44 Å for Ba_2DyTaO_6. The decrease in the lattice parameter was well accounted for on the basis of the ionic size criterion of rare earth ions (15) since Pr ions were replaced by relatively small rare earth ions. The $Ba(Dy_{0.5}Ta_{0.5})O_3$ compound was reported in JCPDS files (Set No. 19-101) as a $A(BB')O_3$-type compound. However, due to the presence of superstructure lines in the XRD pattern of Ba_2DyTaO_6 similar to that of $A_2(BB')O_6$-type ceramics, certainly this compound crystallizes in $A_2(BB')O_6$ complex cubic perovskite crystal structure. Recently, Koshy *et al.* reported the synthesis, dielectric properties of Ba_2RENbO_6 (where RE = Pr, Nd, Sm, and Eu), and their suitability as substrates for YBCO films (3). It is observed that both Ba_2RENbO_6 and Ba_2RETaO_6 compounds are isostructural, having similar characteristic XRD patterns of an ordered double perovskite crystal structure. Wittmann *et al.* reported the ordering in complex perovskites of the type $A_2^{2+}(B^{3+}M^{5+})O_6$, where A^{2+} = Ba, Sr, M^{5+} = Sb, Nb, Ta, and B^{3+} = rare earth, and also obtained cubic perovskite compounds when B^{3+} = Sm, Eu, Gd, Dy, Lu, and Y and A^{2+} = Ba (16). However, the chemical nonreac-

TABLE 1
X-Ray Diffraction Data

Sl. No.	2θ	Width	d(Å)	I/I_0	hkl
		Ba_2PrTaO_6			
1	17.99	0.285	4.927	5	111
2	20.80	0.270	4.267	7	200
3	29.58	0.405	3.018	100	220
4	34.74	0.240	2.580	3	311
5	36.37	0.230	2.468	3	222
6	42.28	0.410	2.136	34	400
7	46.24	0.200	1.962	3	331
8	47.39	0.225	1.917	3	420
9	52.43	0.255	1.744	28	422
10	55.70	0.195	1.646	3	333
11	61.26	0.225	1.512	12	440
12	69.52	0.270	1.351	13	620
13	77.12	0.240	1.236	5	444
14	84.53	0.285	1.145	9	642
		Ba_2NdTaO_6			
1	18.01	0.240	4.921	4	111
2	20.80	0.315	4.267	6	200
3	29.59	0.390	3.017	100	220
4	34.78	0.180	2.577	3	311
5	36.38	0.190	2.468	3	222
6	42.33	0.390	2.133	33	400
7	46.26	0.190	1.960	4	331
8	47.59	0.370	1.909	3	420
9	52.44	0.395	1.743	29	422
10	55.84	0.180	1.645	3	333
11	61.45	0.225	1.508	13	440
12	69.64	0.510	1.349	14	620
13	77.27	0.240	1.234	5	444
14	84.77	0.300	1.143	9	642
		Ba_2EuTaO_6			
1	18.18	0.255	4.876	6	111
2	20.98	0.270	4.231	7	200
3	29.82	0.345	2.944	100	220
4	35.03	0.205	2.559	3	311
5	36.65	0.185	2.450	3	222
6	42.64	0.405	2.119	32	400
7	46.60	0.190	1.947	3	331
8	47.92	0.305	1.987	3	420
9	52.85	0.480	1.731	35	422
10	56.30	0.200	1.634	3	333
11	61.83	0.315	1.499	15	440
12	70.13	0.340	1.341	14	620
13	77.92	0.250	1.225	5	444
14	85.58	0.400	1.134	12	642
		Ba_2DyTaO_6			
1	18.26	0.270	4.855	5	111
2	21.12	0.285	4.203	7	200
3	29.98	0.330	2.978	100	220
4	35.24	0.230	2.545	3	311
5	36.86	0.200	2.440	3	222
6	42.89	0.375	2.107	33	400
7	46.87	0.205	1.936	3	331
8	48.25	0.210	1.887	4	420
9	53.16	0.450	1.722	36	422
10	56.62	0.200	1.624	2	333
11	62.30	0.225	1.489	15	440
12	70.60	0.245	1.333	16	620
13	78.45	0.255	1.218	7	444
14	86.20	0.265	1.127	15	642

tivity of these ceramics with YBCO superconductor and their use as substrates for superconductor films has not been explored so far.

The theoretical density calculated from the lattice parameter, the bulk density determined by the Archimedes method, and the lattice parameter for Ba_2RETaO_6 ceramics are given in Table 2. These materials showed high sinterability and bulk density up to ~97% of theoretical density. The stability and degradation of Ba_2RETaO_6 ceramics under atmospheric conditions were confirmed by humidity treatment. The electrical resistivity and density of humidity treated samples determined after drying were same as those of sintered specimens. This clearly indicated that these compounds showed high stability and no degradation under atmospheric conditions. The resistivity of sintered Ba_2RETaO_6 specimens was $\sim 10^{10}$ Ω cm at room temperature. Well sintered specimens exhibited high mechanical strength and good reflecting surfaces were obtained by mechanical polishing. Organic solvents such as acetone, alcohol, and carbon tetrachloride were used as cleaning agents.

The variations of the dielectric constant (ε') and the loss factor (tan δ) with frequency from 30 Hz to 13 MHz at 77 K for Ba_2RETaO_6 are shown in Figs. 2 and 3 respectively, and Table 3 gives the values of ε' and tan δ at 10 MHz frequency at 77 K. The dielectric constant value of $Ba(Nd_{1/2}Ta_{1/2})O_3$ as reported by Zurmuhlen *et al.* was ~36 at GHz frequencies (17, 18). The Ba_2NdTaO_6 specimen showed the dielectric constant value of ~35 at 10 MHz frequency, which is comparable to the value of ~36 for the $Ba(Nd_{1/2}Ta_{1/2})O_3$

TABLE 2
Values of Lattice Parameter, Theoretical Density, and Bulk Density for Ba_2RETaO_6 Ceramics

Compound	Lattice parameter (Å)	Theoretical density (g/cm^3)	Bulk density (g/cm^3)
Ba_2PrTaO_6	8.552	7.351	6.994
Ba_2NdTaO_6	8.548	7.397	7.072
Ba_2EuTaO_6	8.488	7.641	7.381
Ba_2DyTaO_6	8.441	7.885	7.663

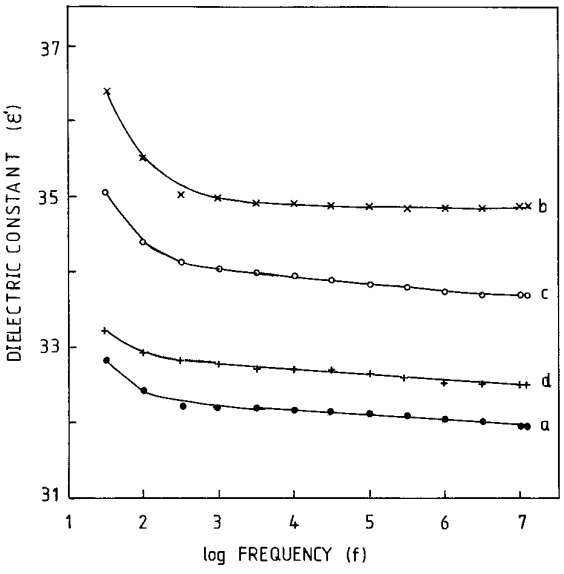

FIG. 2. Variation of dielectric constant (ε') with frequency for (a) Ba_2PrTaO_6, (b) Ba_2NdTaO_6, (c) Ba_2EuTaO_6, and (d) Ba_2DyTaO_6 ceramics at 77 K.

ceramic. Similarly, the dielectric constant values for Ba_2RETaO_6 specimens at MHz frequencies are found to be comparable with those values for Ba_2RENbO_6 at MHz frequencies reported elsewhere (3). It should be noted that the values of ε' and tan δ for Ba_2RETaO_6 at MHz frequency at 77 K are also comparable to those of commonly used substrates such as MgO and $LaAlO_3$ for YBCO films.

The lattice matching of the substrate with YBCO superconductor is one of the important criteria for epitaxial growth of YBCO films on single crystal substrates. The

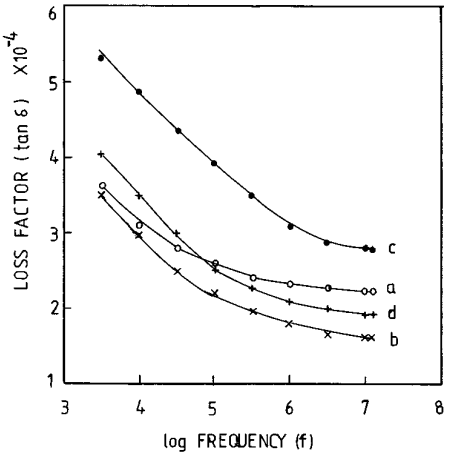

FIG. 3. Variation of loss factor (tan δ) with frequency for (a) Ba_2PrTaO_6, (b) Ba_2NdTaO_6, (c) Ba_2EuTaO_6, and (d) Ba_2DyTaO_6 ceramics at 77 K.

TABLE 3
Values of ε' and tan δ at 10 MHz for Ba_2RETaO_6 Ceramics at 77 K

Compound	Dielectric constant (ε')	Loss factor (tan δ)
Ba_2PrTaO_6	32.0	2.2×10^{-4}
Ba_2NdTaO_6	34.8	1.6×10^{-4}
Ba_2EuTaO_6	33.7	2.8×10^{-4}
Ba_2DyTaO_6	32.5	1.9×10^{-4}

lattice constant values for Ba_2RETaO_6 are found to be in the range from 8.55 to 8.44 Å. Although the lattice matching of these materials with YBCO superconductor is not perfect, taking into account the doubling of the basic perovskite unit cell, lattice constant values are in a range comparable to that of MgO (a = 4.208 Å) which is an extensively used substrate for epitaxial growth of YBCO films. These ceramics showed no phase transitions in the temperature range 300–1373 K as confirmed by DTA measurement. The XRD patterns recorded on melted and subsequently quenched in air Ba_2RETaO_6 specimens were identical to those of sintered samples. This clearly reveals that these ceramics melt congruently and could be grown as single crystals from the melt. Detailed studies on single crystal growth of Ba_2RETaO_6 are in progress.

The chemical nonreactivity of superconductor film with the substrate material at the processing temperature is yet another important criterion for selecting any material as a good substrate. To establish this, the chemical reactivity of YBCO with Ba_2RETaO_6 was studied up to the temperature 1223 K. For this, the composites of 80 vol% YBCO–20 vol% Ba_2RETaO_6 were prepared and pressed pellets were heat treated at 1223 K, followed by annealing at 773 K under flowing oxygen. The XRD patterns recorded for these composites and for pure YBCO are given in Fig. 4. It is noted that the formation of no additional phases was observed in the XRD patterns of composites other than the characteristic peaks due to orthorhombic YBCO and the respective substrate. Further, it is also indicated that YBCO superconductor showed no chemical reaction with Ba_2RETaO_6 ceramics (within the precision of the XRD technique). All the composites showed a superconducting zero resistance transition of 92 K as determined by temperature vs resistivity measurement. Figure 5 shows the temperature vs resistivity plots for all the composites. It is also observed that substantial addition of Ba_2RE TaO_6 up to 20 vol% in YBCO did not affect the superconducting properties of YBCO even after severed heat treatment.

In addition to the favorable dielectric properties and the chemical stability of Ba_2RETaO_6 with YBCO superconductor, the suitability of Ba_2RETaO_6 as substrates for

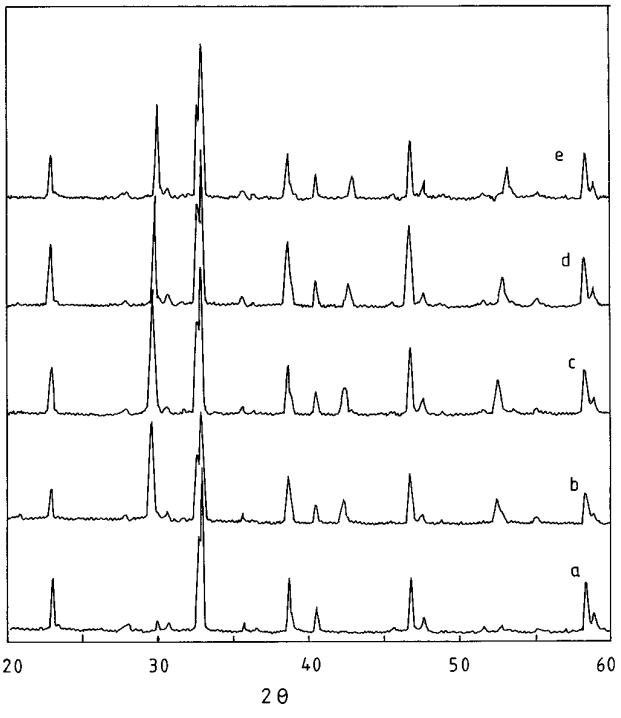

FIG. 4. X-ray powder diffraction patterns of (a) pure YBCO, (b) 80 vol% YBCO–20 vol% Ba_2PrTaO_6, (c) 80 vol% YBCO–20 vol% Ba_2NdTaO_6, (d) 80 vol% YBCO–20 vol% Ba_2EuTaO_6, and (e) 80 vol% YBCO–20 vol% Ba_2DyTaO_6.

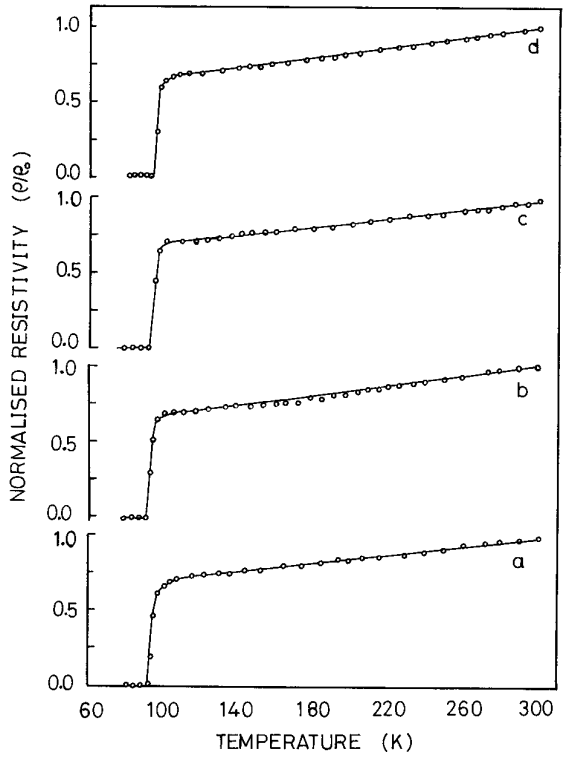

FIG. 5. Temperature vs normalized resistivity curve for the composites. (a) 80 vol% YBCO–20 vol% Ba_2PrTaO_6, (b) 80 vol% YBCO–20 vol% Ba_2NdTaO_6, (c) 80 vol% YBCO–20 vol% Ba_2EuTaO_6, and (d) 80 vol% YBCO–20 vol% Ba_2DyTaO_6. ρ_0 is room temperature resistivity and ρ is resistivity at temperature.

YBCO superconductor film was demonstrated by fabricating a YBCO thick film on these materials by dip coating and partial melting techniques. Thus developed YBCO thick films are found to be textured, showing (00*l*) orientation along with the characteristic peaks of the substrate as seen in the XRD patterns. Figure 6 shows the XRD pattern of a YBCO thick film developed on a Ba_2DyTaO_6 substrate as a representative example. All the thick films showed a superconducting zero resistance transition at 92 K as determined by temperature vs resistance measurement. A plot of temperature vs resistance for the thick film on the Ba_2DyTaO_6 substrate is shown in Fig. 7. High temperature processing of YBCO thick films caused partial melting of film, which facilitated the good adhesion of the film to substrate. Further, the fabrication of YBCO thick films on polycrystalline Ba_2RETaO_6 substrates and the moderately low dielectric constant and loss factor proposes these materials as potential substrates for microwave applications of YBCO superconductor films.

4. CONCLUSIONS

A group of complex cubic perovskites, Ba_2RETaO_6 (where RE = Pr, Nd, Eu, and Dy), were characterized and sintered as single phase materials with high bulk density and stability for the use as potential substrates for microwave applications of YBCO superconducting films. These compounds are found to be isostructural with an ordered

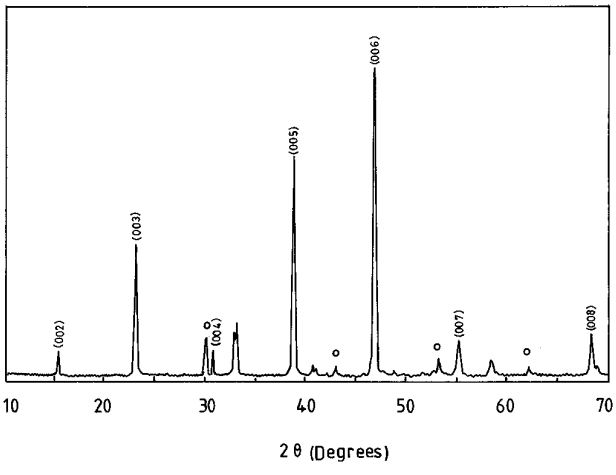

FIG. 6. X-ray diffraction pattern of YBCO thick film on Ba_2DyTaO_6 substrate. Substrate peaks are marked by 'o'.

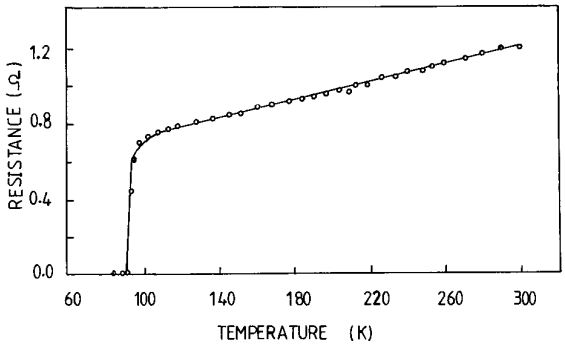

FIG. 7. Temperature vs resistance curve for YBCO thick film on Ba_2DyTaO_6 substrate.

cubic perovskite crystal structure of $A_2(BB')O_6$-type compounds. They melt congruently and growth of single crystals from the melt is possible. The dielectric constant and loss factor values are moderately low and are comparable to those of commercially available substrates such as MgO and $LaAlO_3$. These materials remain chemically stable with YBCO superconductor and substantial addition up to 20 vol% in YBCO does not affect the superconducting properties of YBCO. The YBCO thick films developed on polycrystalline Ba_2RETaO_6 substrates by dip coating and partial melting techniques were textured, showing $(00l)$ orientation with $T_{c(o)}$ of 92 K.

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