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Synthesis and Characterization of Rare-Earth Barium Antimonates,[1] a New Group of Complex Perovskites Suitable as Substrates for $YBa_2Cu_3O_{7-\delta}$ Films

J. Kurian, J. Koshy,[2] P. R. S. Wariar, Y. P. Yadava, and A. D. Damodaran

Regional Research Laboratory, CSIR, Trivandrum 695019, India

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A new group of complex perovskites, REBa$_2$SbO$_6$ (where RE = Pr, Sm, and Gd), have been synthesized and sintered as single phase materials by the solid state reaction method. These materials are found to be isostructural and to have a complex cubic perovskite structure. X-ray diffraction and resistivity measurements have shown that there is no detectable chemical reaction between $YBa_2Cu_3O_{7-\delta}$ and REBa$_2$SbO$_6$ even under severe heat treatment at 950°C and that the addition of REBa$_2$SbO$_6$ up to 20 vol% in $YBa_2Cu_3O_{7-\delta}$ shows no detrimental effect on the superconducting properties of $YBa_2Cu_3O_{7-\delta}$. The dielectric constant and loss factor values of the sintered REBa$_2$SbO$_6$ materials are in a range suitable for their use as substrates for microwave applications. Thick films of $YBa_2Cu_3O_{7-\delta}$ fabricated on polycrystalline REBa$_2$SbO$_6$ substrates give superconducting zero resistivity transition temperature $T_{c(0)}$ = 92 K, indicating the suitability of these materials as substrates for $YBa_2Cu_3O_{7-\delta}$ films. © 1995 Academic Press, Inc.

I. INTRODUCTION

In the course of our research work on the use of mixed oxides of rare-earth elements as substrates for $YBa_2Cu_3O_{7-\delta}$ (YBCO) superconductors (1–3), we have synthesized a new group of complex perovskites, REBa$_2$SbO$_6$ (where RE = Pr, Sm and Gd), having the general formula $A_2(BB')O_6$ (4, 5), which could be used as substrate materials for YBCO superconductors. In this paper, we report the synthesis and sintering of REBa$_2$SbO$_6$ as single phase materials for the first time. The structure and dielectric properties of REBa$_2$SbO$_6$ and their suitability as substrate materials for YBCO films are also discussed.

II. EXPERIMENTAL PROCEDURE

REBa$_2$SbO$_6$ were prepared by mixing stoichiometric amounts of high purity (99.9%) rare earth oxides, $BaCO_3$, and Sb_2O_3, followed by calcination at 1200°C for 24 hr with three intermediate grindings. The calcined materials were pressed into pellets with dimensions of 10 mm diameter and 1.5 mm thickness. These pellets were sintered in air at temperatures between 1500 and 1550°C for 12 hr. The structure of the compounds was studied by X-ray diffraction (XRD) (Rigaku, Japan) using nickel-filtered Cu$K\alpha$ radiation. The dielectric constant and loss factor of REBa$_2$SbO$_6$ at MHz frequencies were measured using a complex impedance analyzer (HP 4192A, U.S.A.). For chemical reactivity studies, REBa$_2$SbO$_6$ and YBCO powder (prepared from high purity Y_2O_3, $BaCO_3$, and CuO by the solid state reaction method) were mixed in a 1 : 1 volume ratio and pressed into pellets. These pellets were heated at 950°C in air for 15 hr and their chemical reactivity was studied by X-ray powder diffraction. The effect of REBa$_2$SbO$_6$ addition on the superconductivity of YBCO was examined by resistivity–temperature measurements. The resistance measurements were made by the four probe method using a nanovoltmeter (Model 181, Keithley Instruments Inc., Cleveland) and a current source (Model 220, Keithley Instruments Inc.). The temperature of the samples was measured by a copper constantan thermocouple, calibrated with a RF-800 rhodium–iron resistance sensor, with an accuracy of ±0.2 K.

In order to examine the suitability of REBa$_2$SbO$_6$ materials as substrates for YBCO superconductor films, YBCO thick films were fabricated on REBa$_2$SbO$_6$ substrates by screen-printing. The thick film paste of YBCO was made by mixing superconducting YBCO powder with isopropyl alcohol and its viscosity was controlled by the addition of commercially available fish oil. This paste was screen-printed on highly polished polycrystalline REBa$_2$SbO$_6$ using a screen of 325 mesh size. The screen-printed films were heated in a programmable furnace in air at a rate of 5°C/min to 980°C. These films were cooled at 0.2°C/min to 940°C, kept at this temperature for 30 min, and then cooled to room temperature at 2°C/min. Heating to 980°C was necessary to get good adhesion of

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[2] To whom correspondence should be addressed.

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the film to the substrate and slow cooling at 2°C/min was essential for oxygenation. More details of the screen-printing process are given in Ref. (6). The structure of the screen-printed YBCO films on *RE*Ba_2SbO_6 substrates was examined by XRD and the superconductivity of the thick films was studied by temperature–resistance measurements.

As single crystals are needed for substrate applications, melting experiments were carried out to examine whether *RE*Ba_2SbO_6 materials melt congruently for possible single crystal growth from melt. Single phase *RE* Ba_2SbO_6 powder was placed in a platinum crucible and the material was melted completely in air at a temperature of 1750°C, using a muffle furnace. The melted samples were withdrawn from the furnace and quenched in air to room temperature. The quenched samples were then examined by X-ray diffraction. The differential thermal analysis of *RE*Ba_2SbO_6 samples was carried out in the temperature range 30–1350°C under nitrogen using a computerized Shimadzu DTA-50H (Japan) instrument.

III. RESULTS AND DISCUSSION

The XRD patterns of sintered $PrBa_2SbO_6$, $SmBa_2SbO_6$, and $GdBa_2SbO_6$ for 2θ values between 5 and 90° are shown in Fig. 1. The computerized data for these materials are given in Table 1. The XRD patterns and XRD data clearly show that all these materials have the same structure, as judged by the similarity in intensities and positions of the lines on the powder X-ray patterns. *RE*Ba_2SbO_6 are also found to be isostructural with other rare-earth cubic perovskites with the general formula $A_2(BB')O_6$, such as $EuBa_2NbO_6$ and YBa_2NbO_6, reported in the JCPDS file, in which doubling of the basic perovskite unit cell is observed. The doubling of the basic perovskite unit cell in these materials is due to the ordering of B and B' on the octahedral sites, exhibited in the XRD pattern by the presence of superstructure lines (7). The presence of superstructure lines in the XRD patterns shown in Fig. 1 thus indicates the ordering of the basic ABO_3 perovskite unit cell in the *RE*Ba_2SbO_6 materials. The crystal structure diagram of *RE*Ba_2SbO_6 is shown in Fig. 2. The XRD peaks including the minor peaks for *RE*Ba_2SbO_6 are now indexed for a complex cubic perovskite structure. Theoretical densities of *RE*Ba_2SbO_6 were calculated from the lattice constant values and sintered densities were measured by the Archimedes method. Lattice constant, theoretical density, and sintered density of *RE*Ba_2SbO_6 are given in Table 2. The sintered samples are single phase with sintered density >97%. The DTA curves of these samples did not show any phase transition up to a temperature of 1350°C. These materials are highly stable under atmospheric conditions and no degradation was observed in the stability of the samples, even if they were kept in boiling water for 1 hr. The samples were mechanically strong and could be sliced into pieces of 0.5 mm thickness with a diamond cutter. Good reflecting surfaces were obtained by mechanical polishing and organic solvents such as alcohol, acetone, and carbon tetrachloride could be used as effective cleaning agents. The resistivity of *RE*Ba_2SbO_6 is ~10^{10} ohm cm at room temperature.

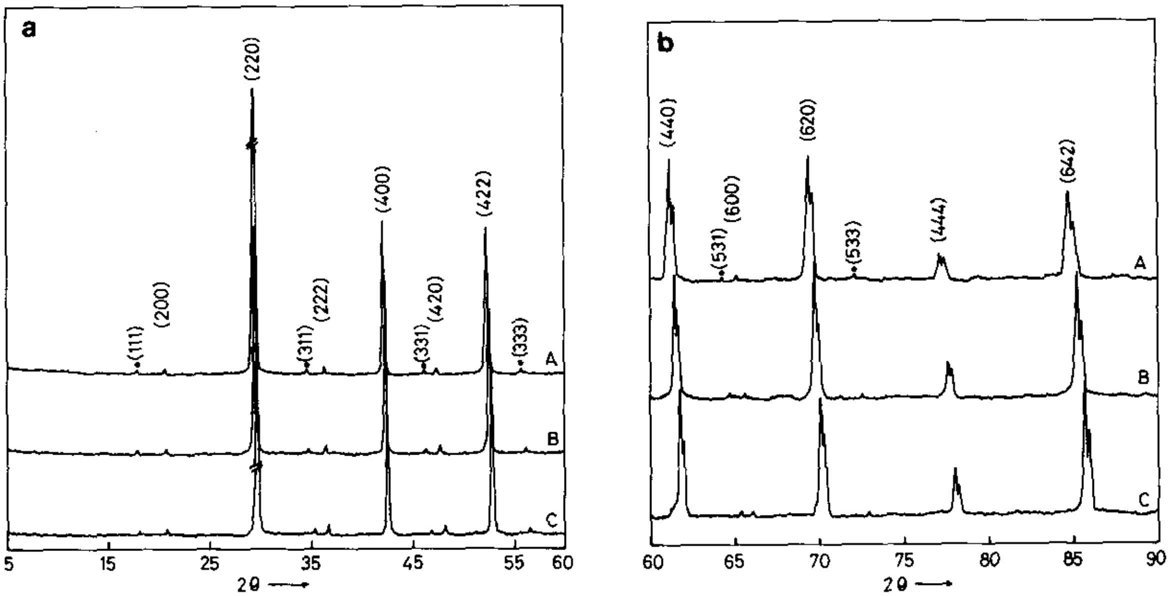

FIG. 1. X-ray diffraction patterns of phase pure sintered (A) $PrBa_2SbO_6$, (B) $SmBa_2SbO_6$ and (C) $GdBa_2SbO_6$. (a) 2θ from 5 to 60° and (b) 2θ from 60 to 90°. The superstructure lines are marked by "•."

TABLE 1
X-Ray Diffraction Data for REBa$_2$SbO$_6$

Sl. no.	2θ	Width	'd'	I/I_0	hkl
		$PrBa_2SbO_6$			
1	17.900	0.165	4.951	2	111
2	20.640	0.240	4.300	2	200
3	29.410	0.510	3.035	100	220
4	34.630	0.195	2.588	2	311
5	36.310	0.435	2.472	3	222
6	42.140	0.510	2.143	32	400
7	46.190	0.210	1.963	2	331
8	47.380	0.495	1.917	3	420
9	52.260	0.585	1.749	34	422
10	55.760	0.185	1.647	2	333
11	61.210	0.600	1.513	14	440
12	64.210	0.240	1.449	2	531
13	65.220	0.240	1.429	2	600
14	69.380	0.615	1.353	15	620
15	72.180	0.195	1.307	2	533
16	77.060	0.555	1.237	5	444
17	84.620	0.840	1.144	12	642
		$SmBa_2SbO_6$			
1	17.980	0.195	4.929	2	111
2	20.830	0.210	4.261	2	200
3	29.600	0.420	3.016	100	220
4	34.920	0.225	2.567	2	311
5	36.540	0.330	2.457	3	222
6	42.410	0.435	2.130	36	400
7	46.400	0.180	1.955	2	331
8	47.700	0.375	1.905	3	420
9	52.630	0.480	1.738	33	422
10	56.010	0.180	1.6405	2	333
11	61.590	0.450	1.505	14	440
12	64.74	0.165	1.438	2	531
13	65.70	0.165	1.420	2	600
14	69.830	0.585	1.346	15	620
15	72.72	0.195	1.299	2	533
16	77.69	0.315	1.228	5	444
17	85.280	0.345	1.137	14	642
		$GdBa_2SbO_6$			
1	18.01	0.165	4.921	2	111
2	20.90	0.180	4.247	3	200
3	29.71	0.390	3.005	100	220
4	35.00	0.315	2.562	2	311
5	36.69	0.300	2.447	5	222
6	42.58	0.390	2.122	32	400
7	46.62	0.240	1.946	2	331
8	47.89	0.337	1.898	4	420
9	52.85	0.450	1.731	37	422
10	56.32	0.165	1.632	2	333
11	61.84	0.570	1.499	15	440
12	64.92	0.210	1.435	2	531
13	66.09	0.195	1.413	3	600
14	70.15	0.600	1.340	15	620
15	72.99	0.180	1.295	2	533
16	78.04	0.480	1.233	8	444
17	85.71	0.570	1.133	16	642

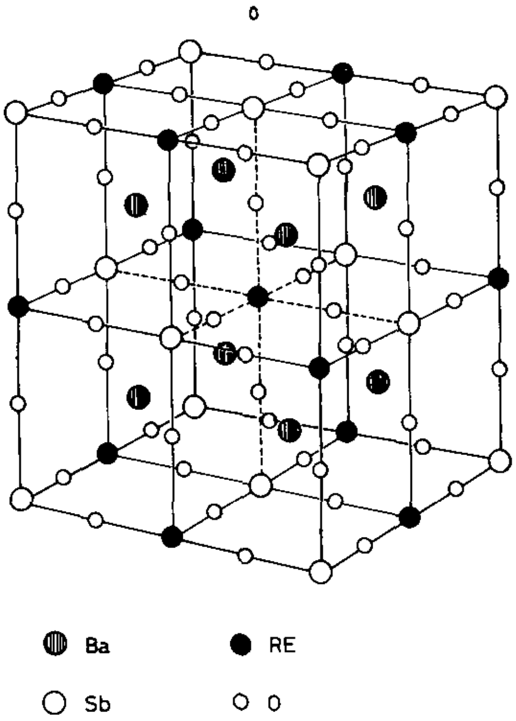

FIG. 2. Crystal structure diagram of REBa$_2$SbO$_6$.

The dielectric constant (ε') and loss factor ($\tan\delta$) of polycrystalline REBa$_2$SbO$_6$ (sintered density >97%) were studied in the frequency range from 30 Hz to 13 MHz at room temperature and the variation of ε' and $\tan\delta$ with frequency are shown in Figs. 3 and 4 respectively. The ε' and $\tan\delta$ values of REBa$_2$SbO$_6$ measured at 10 MHz at room temperature are given in Table 3. The dielectric constant and loss factor values for REBa$_2$SbO$_6$ at MHz frequencies are comparable to those of commonly used substrates such as MgO and $LaAlO_3$ for YBCO films.

In addition to favorable dielectric properties, the lattice matching of REBa$_2$SbO$_6$ with YBCO is also an important factor for epitaxial growth of YBCO films on single crystal substrates. REBa$_2$SbO$_6$ have a complex cubic perovskite structure with lattice constants between 8.488 and 8.572 Å (Table 2). Even though the lattice matching

TABLE 2
Lattice Constant, Theoretical Density, and Sintered Density of REBa$_2$SbO$_6$

Material	Lattice constant (a) Å	Theoretical density g/cm³	Sintering temperature °C	Sintered density g/cm³
$PrBa_2SbO_6$	8.572	6.676	1500	6.482
$SmBa_2SbO_6$	8.520	6.901	1550	6.742
$GdBa_2SmO_6$	8.488	7.054	1530	6.856

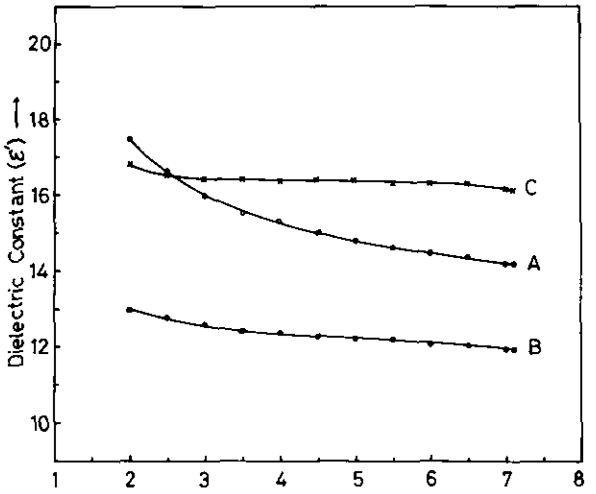

FIG. 3. Variation of dielectric constant (ε′) with frequency for (A) $PrBa_2SbO_6$, (B) $SmBa_2SbO_6$ and (C) $GdBa_2SbO_6$.

of these materials with YBCO is not perfect, the lattice constant values of $RE$$Ba_2SbO_6$, based on the doubling of the simple perovskite unit cell, are in a range comparable to that of MgO (a = 4.208 Å), which is an extensively used substrate for epitaxial growth of YBCO films. The XRD patterns taken on the melted and subsequently quenched $RE$$Ba_2SbO_6$ samples are identical to those of sintered samples, indicating that these materials melt congruently and could be grown from the melt as single crystals. Detailed studies of single crystal growth of $RE$$Ba_2SbO_6$ are in progress and will be reported in due course.

One of the most important criteria for the selection of any material as a substrate for YBCO superconductors is chemical nonreactivity between the substrates and the film at the processing temperature. In order to see whether $RE$$Ba_2SbO_6$ is chemically compatible with YBCO, the chemical reactivity of $RE$$Ba_2SbO_6$ with YBCO was studied at temperatures up to 950°C. Superconducting YBCO powder was mixed with $RE$$Ba_2SbO_6$ in a 1 : 1 volume ratio and pressed into pellets. The pellets were then annealed at 950°C for 15 hr and cooled slowly. If YBCO reacted with $RE$$Ba_2SbO_6$ under such annealing conditions, additional phases besides YBCO and $RE$$Ba_2SbO_6$ or change in lattice constants would be observed in the X-ray diffraction patterns. On the other hand, if YBCO does not react with $RE$$Ba_2SbO_6$, the crystalline phases after annealing will be just two identical phases of YBCO and $RE$$Ba_2SbO_6$.

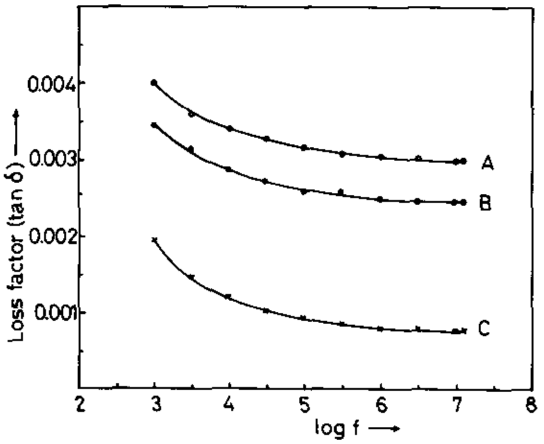

FIG. 4. Variation of loss factor (tan δ) with frequency for (A) $PrBa_2SbO_6$, (B) $SmBa_2SbO_6$ and (C) $GdBa_2SbO_6$.

TABLE 3

Dielectric Constant (ε′) and Loss Factor (tan δ) of $RE$$Ba_2SbO_6$ at 10 MHz at Room Temperature

Material	Dielectric constant (ε′)	Loss factor (tan δ)
$PrBa_2SbO_6$	14.2	2.9×10^{-3}
$SmBa_2SbO_6$	12.0	2.5×10^{-3}
$GdBa_2SbO_6$	16.1	8×10^{-4}

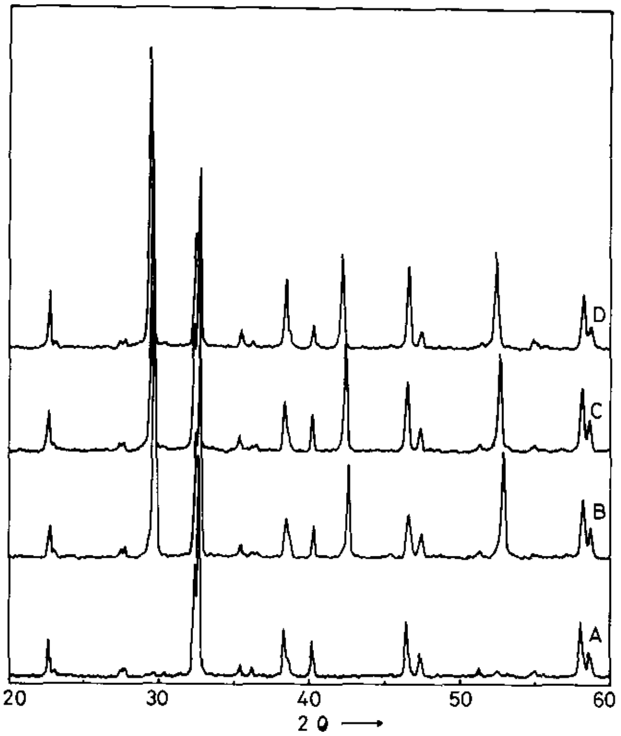

FIG. 5. X-ray diffraction patterns of (A) pure YBCO, (B) 1 : 1 volume mixture of YBCO and $GdBa_2SbO_6$, (C) 1 : 1 volume mixture of YBCO and $SmBa_2SbO_6$, and (D) 1 : 1 volume mixture of YBCO and $PrBa_2SbO_6$, all annealed at 950°C for 15 hr.

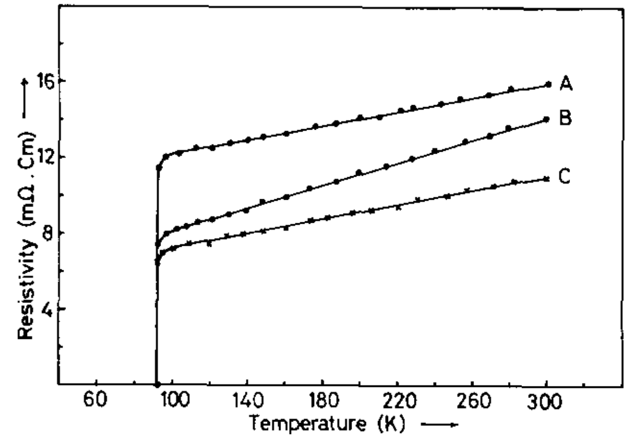

FIG. 6. Resistivity–temperature curves for YBCO–*RE*Ba_2SbO_6 composites containing 20 vol% of (A) $PrBa_2SbO_6$, (B) $SmBa_2SbO_6$, and (C) $GdBa_2SbO_6$, all annealed at 950°C for 15 hr.

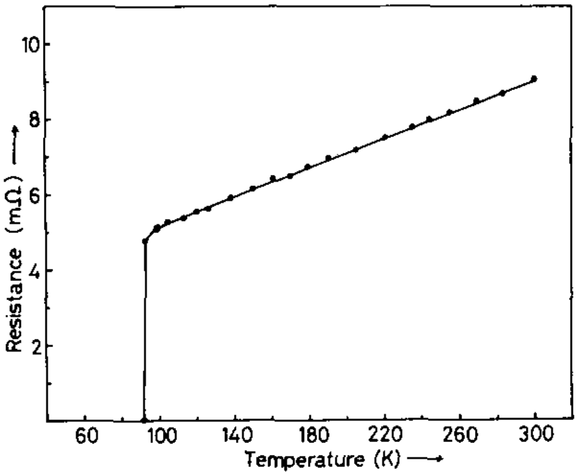

FIG. 8. Temperature–resistance curve of screen-printed $YBa_2Cu_3O_{7-\delta}$ thick film on $GdBa_2SbO_6$ substrate.

Powder diffraction patterns of an annealed sample of YBCO and *RE*Ba_2SbO_6 are shown in Fig. 5. X-ray diffraction patterns of the two phases in the annealed samples (Figs. 5B–5D) were compared with those of pure BYCO (Fig. 5A) and pure *RE*Ba_2SbO_6 (Fig. 1). It is clear from these figures (5B–5D) that no new phase was formed (within the precision of the powder XRD technique) in the YBCO–*RE*Ba_2SbO_6 composites. This indicates that no detectable chemical reaction takes place between YBCO and *RE*Ba_2SbO_6 even under severe heat treatment. The effect of *RE*Ba_2SbO_6 addition on the superconductivity of YBCO was studied by resistivity–temperature measurements. Figure 6 shows the resistivity vs temperature curves for YBCO–*RE*Ba_2SbO_6 composite system containing 20 vol% of *RE*Ba_2SbO_6 annealed at ~950°C for 15 hr. A superconducting transition temperature of 92 K in all these composite samples indicates that a substantial addition of *RE*Ba_2SbO_6 in YBCO did not have any detrimental effect on the superconducting transition temperature of YBCO even after severe heat treatment.

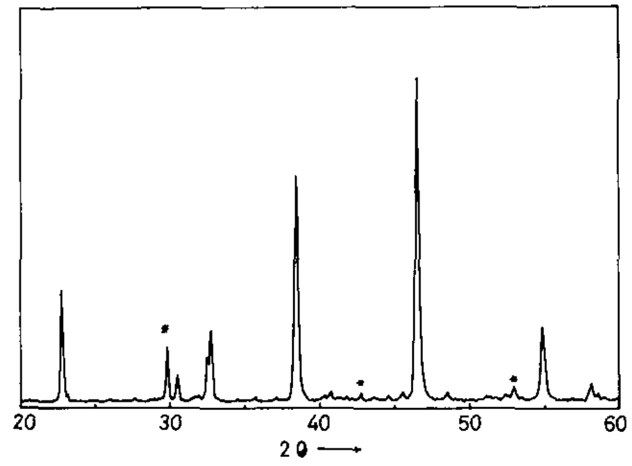

FIG. 7. X-ray diffraction pattern of screen-printed $YBa_2Cu_3O_{7-\delta}$ thick film on $GdBa_2SbO_6$ substrate. (Substrate peaks are marked by "*.")

In order to examine the suitability of *RE*Ba_2SbO_6 as substrates for YBCO superconductor, a YBCO thick film was screen-printed on these substrates. Figure 7 shows the X-ray pattern of a thick film developed on $GdBa_2SbO_6$ substrate as a typical example. Except for the characteristic peaks of $GdBa_2SbO_6$, all other XRD peaks in Fig. 7 are due to orthorhombic superconducting YBCO. Figure 8 shows a representative temperature–resistance curve of a screen-printed YBCO thick film on $GdBa_2SbO_6$ substrate. The film showed metallic behavior in the normal state and gave a zero resistivity superconducting transition temperature $T_{c(o)} = 92$ K with a transition width of ~2 K. Because of the high processing temperature (~980°C) and the partial melting of the YBCO film in the screen printing process, YBCO films adhered very well to the *RE*Ba_2SbO_6 substrates. A peel-off test carried out using a highly adhesive tape confirmed the excellent adhesion of the YBCO film to the substrate.

IV. CONCLUSION

Three new materials, $PrBa_2SbO_6$, $SmBa_2SbO_6$, and $GdBa_2SbO_6$, have been synthesized, characterized, and sintered as single phase materials by the solid state reaction method. These materials are isostructural and have an ordered cubic perovskite structure of type $A_2(BB')O_6$. The presence of superstructure lines in the XRD patterns of *RE*Ba_2SbO_6 indicates the ordering of the basic ABO_3 perovskite unit cell. The dielectric constant and loss factor of the sintered pellets are comparable to those of the MgO and $LaAlO_3$ substrates commonly used for YBCO films. The melting experiments showed that $RE\mathrm{Ba_2SbO_6}$ melts congruently and therefore can be grown as single crystals from the melt. YBCO does not react with RE $\mathrm{Ba_2SbO_6}$ even after a 1 : 1 volume mixture is annealed at 950°C for 15 hr. Addition of $RE\mathrm{Ba_2SbO_6}$ up to 20 vol% in YBCO did not show any detrimental effect on the superconducting property of YBCO. The use of $RE\mathrm{Ba_2SbO_6}$ as a substrate material was demonstrated by screen-printing a superconducting YBCO thick film ($T_{c(o)} = 92$ K) onto these polycrystalline substrates.

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