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$BaZrO_3$ and $BaHfO_3$: preparation, properties and compatibility with $YBa_2Cu_3O_{7-x}$

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Single-phase $BaZrO_3$ and $BaHfO_3$ polycrystalline powders were prepared by solid-state reaction and by spray-drying methods. $BaHfO_3$ ceramic was fabricated at 1300 °C for 24 h after pre-sintering HfO_2 and $BaCO_3$ powders at 1040 °C for 4 h. Homogeneous powders of $BaZrO_3$ and $BaHfO_3$ were also prepared by a spray-drying route. The interaction between $YBa_2Cu_3O_{7-x}$ (YBCO) and $BaHfO_3$ and $BaZrO_3$ was investigated in the temperature range 900–1060 °C using heat-treatment cycles appropriate to composite reaction processing and melt-texturing. The results indicate that neither compound reacts significantly with YBCO at 950 °C, and $BaHfO_3$ is still unreactive up to 1000 °C. Both of them are also very stable during the melting-texture process. $BaHfO_3$ and $BaZrO_3$ are thus very promising substrate materials and buffer layers for the deposition of thin and thick films and as container materials for bulk YBCO superconductors; $BaHfO_3$ seems to be a more stable material than $BaZrO_3$.

1. Introduction

The fabrication of thin- or thick-film high-temperature superconductors on suitable substrates has become a major challenge in the development of many electronic applications because of the high reactivity of the $YBa_2Cu_3O_{7-x}$ (YBCO) system which may arise from the highly electropositive Ba^{2+} ions. Because films are in intimate contact with substrates and have large area-to-volume ratios, they are susceptible to contamination from the substrates. The typically high process temperatures for the deposition of films aggravates the problem because of increased diffusion rates. The search for suitable substrate materials for the fabrication of thin films has led to extensive studies of the reaction between YBCO and various substrate materials: non-metallic substrates silicon, Al_2O_3, ZrO_2, MgO, MgF_2, CeO_2, $NdGaO_3$, $LaAlO_3$, $BaZrO_3$ and $SrTiO_3$ as well as the metallic substrates silver, copper, niobium, etc. [1–7]. Currently, MgO- and Y_2O_3-stabilized ZrO_2 (YSZ) substrates are widely used for the deposition of thin films. However, when YBCO films were grown *in situ* on (0 0 1)-oriented YSZ single-crystal substrate by electron-beam evaporation, a crystalline intermediate layer (about several nanometres) between the YBCO film and YSZ substrate was observed by high-resolution electron microscopy (HREM). It was shown by energy-dispersive X-ray (EDX) to be a barium-enriched phase, possibly barium zirconate, formed by the reaction [8]. Chemical reaction study also suggested that YSZ did react with YBCO, but one of the products, $BaZrO_3$, appears to have inhibited further reactions [4], which might suggest that $BaZrO_3$ is a compatible material with YBCO.

Recently, $BaZrO_3$ has been prepared by a sol–gel route involving mixing of barium hydroxide dissolved in methanol and zirconium propoxide [9]. Drying at 110 °C results in the formation of an agglomerated amorphous powder, which is milled prior to calcination. Calcination at temperatures above 620 °C results in $BaZrO_3$. The interaction between $BaZrO_3$ and YBCO was investigated and the results show that $BaZrO_3$ could be an inert material to YBCO.

In view of the similarity of zirconium and hafnium in terms of the structure and properties of elements, oxides and compounds, we have investigated the interaction between the superconductor and $BaHfO_3$ to explore the possibility of using $BaHfO_3$ as a potentially new non-reactive substrate material.

Traditional multiple-component ceramic powder processing usually incorporates solid-state reactions to produce a desired compound. Because the degree of component mixing in the precursor is determined by the largest individual particle and the microscale homogeneity, when the precursor powder is calcined, the resulting material may contain secondary phases and unreacted compositions. In addition, a high sintering temperature is normally needed to prepare ceramic compounds by solid-state reaction routes, especially for the synthesis of some compounds with high melting points, such as $BaZrO_3$ and $BaHfO_3$. Spray-drying is a process by which a fluid feed material is transfered into a dry powder by spraying the feed into a hot drying medium. It is an economical and continuous operation which can produce a powder of uniform and reproducible character. Therefore, the spray-drying technique was also used to prepare $BaXO_3$ (X = Zr, Hf) in order to solve problems associated with the solid-state reaction method.

In the present study, single-phase $BaHfO_3$ and $BaZrO_3$ polycrystalline powders were prepared by both a solid-state reaction and a spray-drying method.

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The interaction between YBCO and $BaHfO_3$ and $BaZrO_3$ was investigated in the temperature range 900–1060 °C using heat-treatment cycles appropriate to composite reaction processing and melt-texturing. The compatibility between YBCO and $BaZrO_3$ and $BaHfO_3$ has been investigated and is discussed.

2. The synthesis of $BaZrO_3$

2.1. Solid-state reaction method

$BaZrO_3$ has a cubic perovskite-type structure with a crystal lattice constant of 0.419 29 nm. Its density is 6.229 at 26 °C. Some study of the reaction between $BaCO_3$ and ZrO_2 showed that the formation of barium zirconate in the $BaCO_3 + ZrO_2$ system begins at 600 °C, that its concentration under equilibrium conditions amounts to 15.8% at 900 °C, and 63.9% at 1050 °C, and that the formation of $BaZrO_3$ is almost complete at 1300 °C. The synthesis temperature could be lowered by the thermal decomposition of jointly precipitated compounds of $BaCO_3$ and $ZrO(OH)_2$ [10]. The barium zirconate used for the NBS XRD data pattern was prepared by heating $BaCO_3$ and ZrO_2 for 1 h at 1550 °C [11].

In our experiment, $BaCO_3$ (Johnson Matthey) and ZrO_2 (Aldrich) were used as the starting materials. The $BaZrO_3$ were obtained by heating a powder mixture of $BaCO_3 + ZrO_2$ at 1170 °C for 10 h, and the X-ray diffraction pattern is shown in Fig. 1.

2.2. Spray-drying method

$BaZrO_3$ powders were prepared from a spray-drying aqueous solution of barium nitrate and zirconyl nitrate hydrate (obtained from Aldrich, UK). $Ba(NO_3)_2$ and $ZrO(NO_3)_2 \cdot 2H_2O$ were dissolved in distilled water to yield a Ba:Zr atomic ratio of 1:1. Spray-drying consisted of atomizing the solution in a chamber of hot swirling air using a Buchi 190 spray dryer. The dried and partially decomposed salts were carried in the air stream through the outlet of the chamber and collected in a glass container. The inlet and outlet temperatures during spray-drying were about 220 and 140 °C, respectively.

The calcination temperature was determined by differential thermal analysis and thermogravimetric analysis (DTA–TG) using a STA-780 Series Thermal Analyser, and the X-ray diffraction (XRD) analysis was carried out using CuK_α radiation. The DTA + TG diagram of the $BaZrO_3$ powders from spray-drying is depicted in Fig. 2. X-ray diffraction shows that the exothermic peak and the maximum weight loss rate at about 580 °C indicates the formation of $BaZrO_3$. To speed up the reaction process, the $BaZrO_3$ powder was calcined at 800 °C for 4 h, and the corresponding XRD pattern is shown in Fig. 3. As can be seen from the diagram, single cubic phase $BaZrO_3$ is obtained and the calculated crystal lattice constant is 0.4192 nm.

3. The synthesis of $BaHfO_3$

3.1. Solid-state reaction method

$BaHfO_3$ has a cubic perovskite type structure with a crystal constant of 0.4171 nm [12]. The reaction of hafnium dioxide with the oxides of the alkaline earth metals has been studied very little. Godina and Keler [13] described the reaction of HfO_2 with SrO and

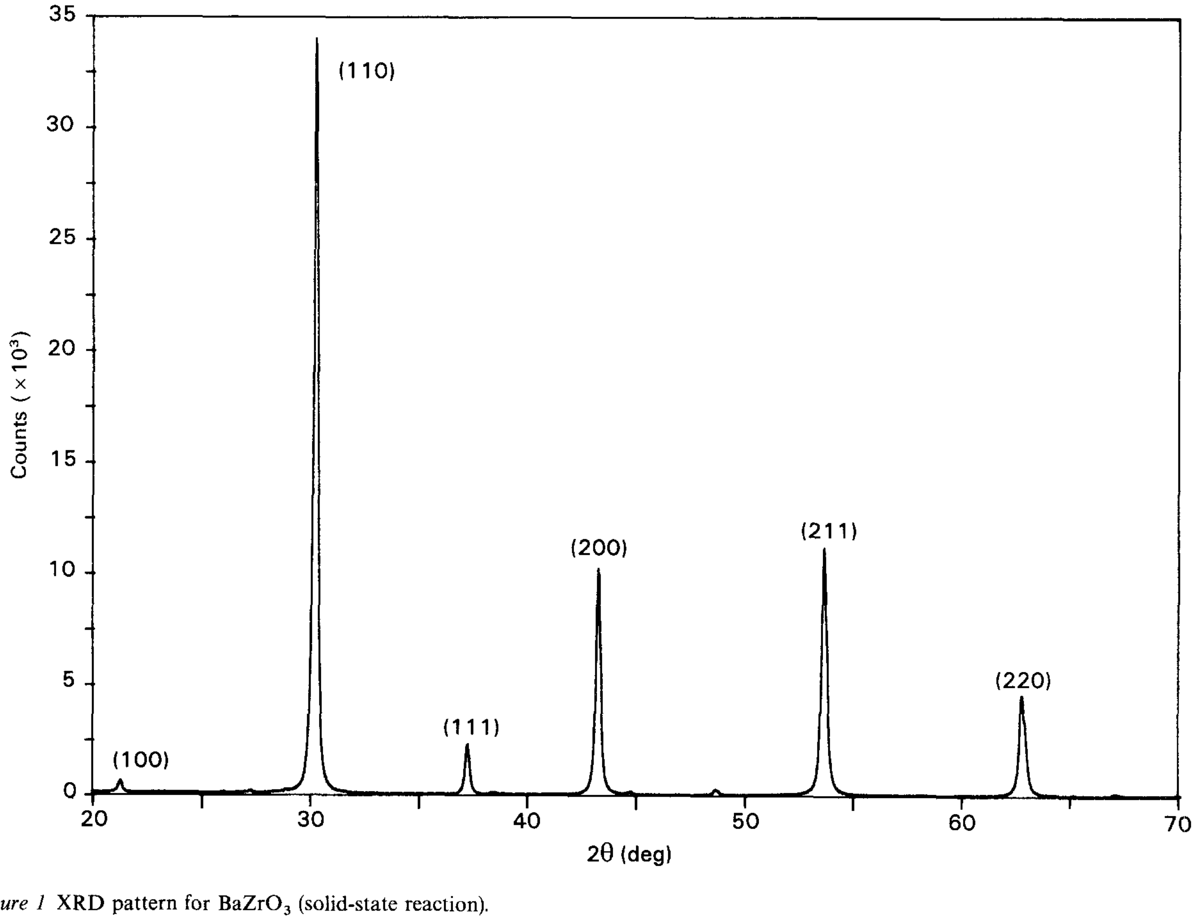

Figure 1 XRD pattern for $BaZrO_3$ (solid-state reaction).

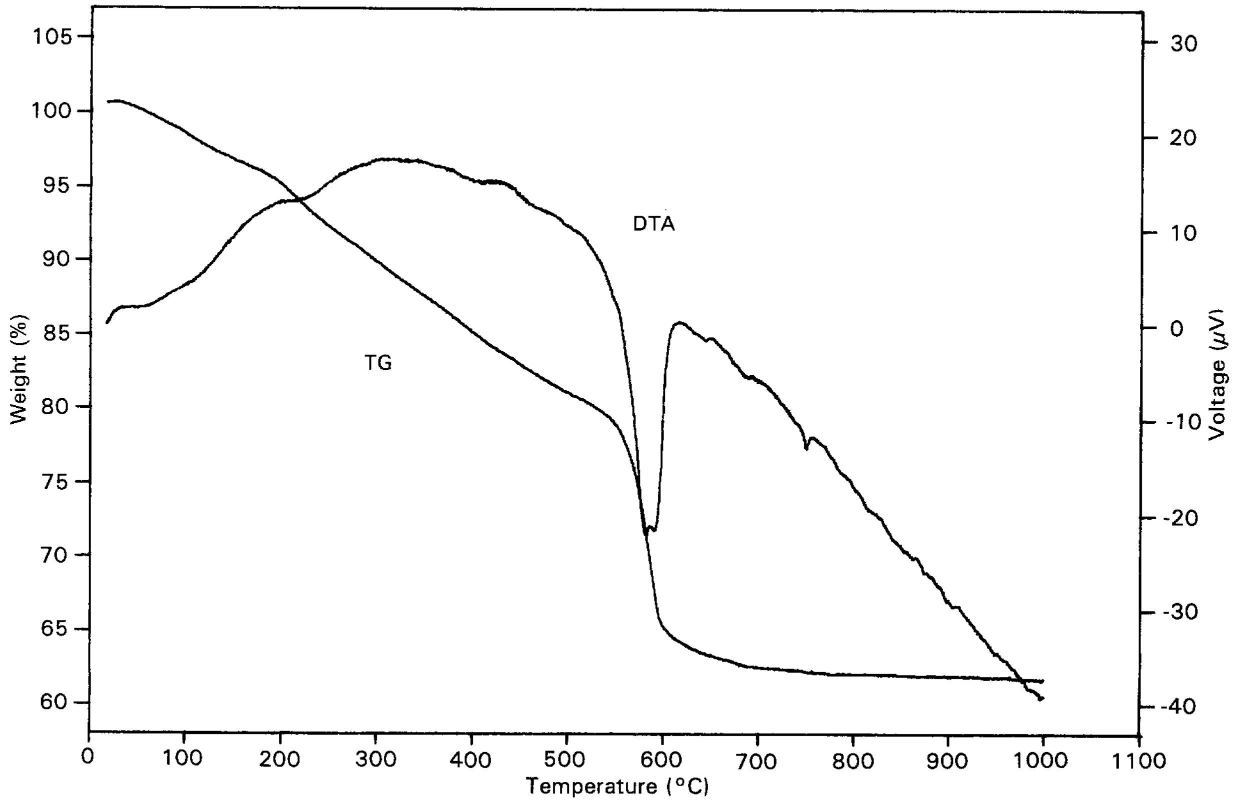

Figure 2 DTA + TG diagram for $BaZrO_3$ powder prepared by spray-drying.

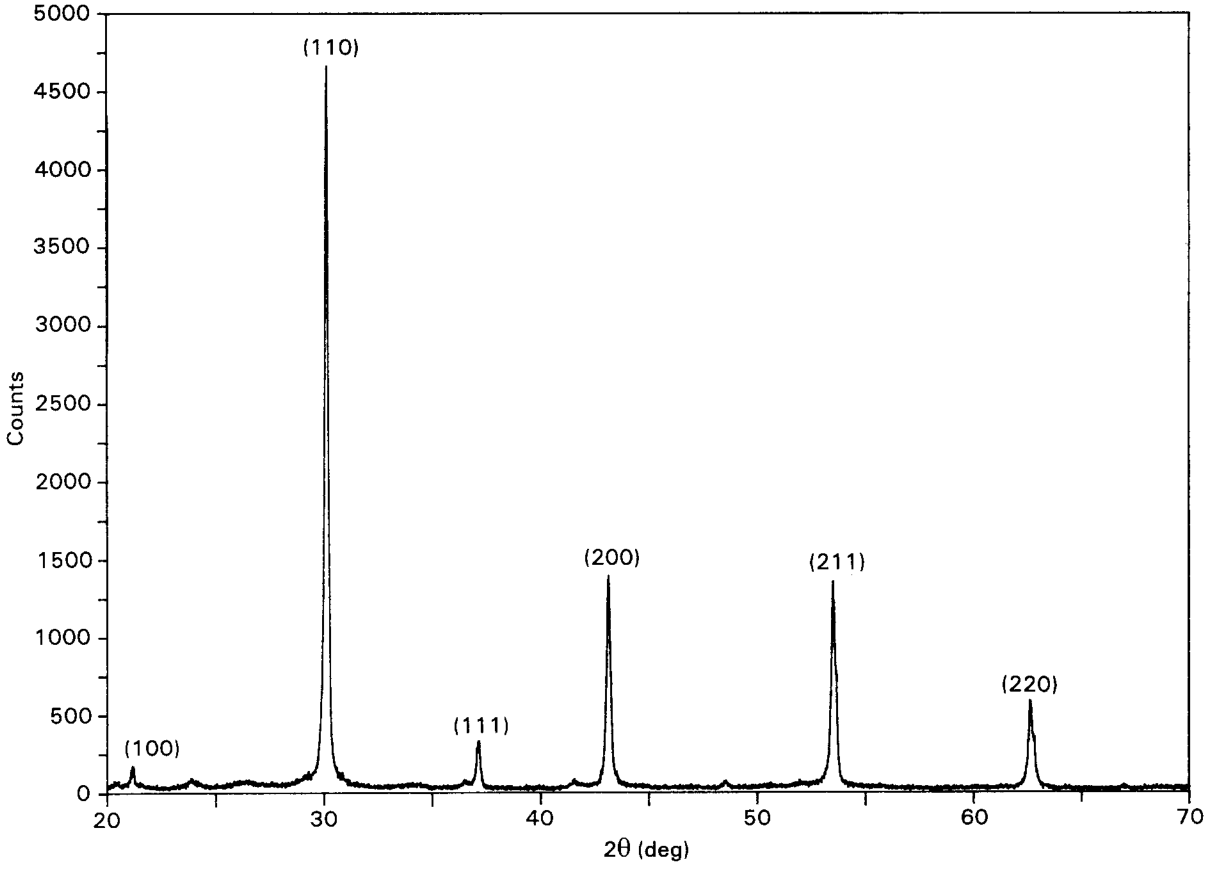

Figure 3 XRD pattern for $BaZrO_3$ (spray-drying method).

BaO. They noted that a particularly rapid reaction occurs between HfO_2 and $BaCO_3$ at 1100 °C, and that a 95% yield of $BaHfO_3$ is obtained after 1 h. Turlier and Prettre [14] suggested that the rate of reaction between $BaCO_3$ and HfO_2 reaches a maximum at 900 °C, and a complete transformation to $BaHfO_3$ occurs at 1270 °C.

In our present work, $BaHfO_3$ is synthesized using $BaCO_3$ and HfO_2 (Johnson Matthey) as raw materials. To study the synthesis mechanism, and to determine the suitable calcination temperature of $BaHfO_3$, differential scanning calorimetry (DSC) and X-ray diffraction were carried out. The DSC analysis was conducted from room temperature to 1100 °C on a NETZSCH DSC-404 analyser of $BaCO_3$ and HfO_2 powder using a heating rate of $10\ °C\,min^{-1}$.

The XRD was conducted for the $BaCO_3 + HfO_2$ powders sintered at 900 and 1040 °C, respectively, for 4 h, and the XRD pattern was shown in Fig. 4. The $BaHfO_3$ ceramic was synthesized at 1300 °C for 24 h after calcining $BaCO_3$ and HfO_2 powders at 1040 °C for 4 h.

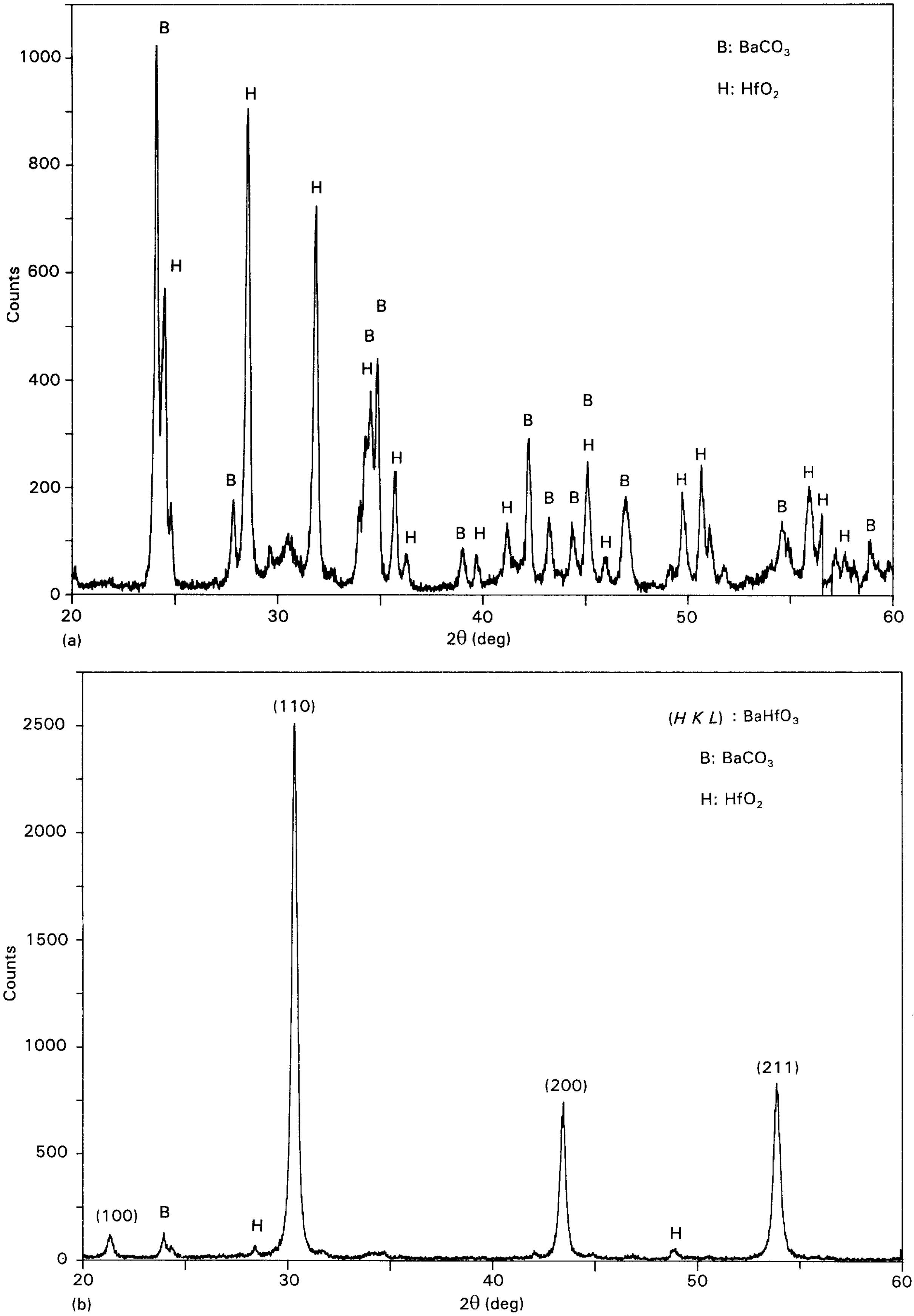

Figure 4 XRD patterns for (a) $BaCO_3 + HfO_2$ reacted at 900 °C for 4 h, and (b) $BaCO_3 + HfO_2$ reacted at 1040 °C for 4 h.

Two endothermic peaks at 800 and 990 °C were observed in a DSC trace for a 1:1 mixture of $BaCO_3$ and HfO_2. XRD analysis shows that no reaction occurs between $BaCO_3$ and HfO_2 when the temperature is below 900 °C, whereas $BaHfO_3$ is obtained at 1040 °C for 4 h. This suggests that the endothermic peak at 990 °C is the result of the formation of $BaHfO_3$ from $BaCO_3$ and HfO_2. Therefore, we select 1040 °C as the calcination temperature and 1300 °C as the sintering temperature.

Fig. 5 shows the XRD pattern of $BaHfO_3$ ceramic sintered at 1300 °C for 24 h. It has been found that a single-phase $BaHfO_3$ is formed. The crystal lattice constant of $BaHfO_3$ is calculated as $a = 0.4171$ nm.

3.2. Spray-drying method

Because hafnium is quite stable and hafnium nitrate is not available, hafnium oxychloride was used instead. The solution for spray drying was prepared by dissolving $HfOCl_2 \cdot 8H_2O$ and $BaCO_3$ in distilled water by adding HCl to obtain a Ba:Hf atomic ratio of 1:1. The spray-drying process consisted of atomizing the solution in a container of swirling hot air, followed by a drying step using a Buchi 190 Spray Dryer. Differential thermal analysis, thermogravimetric analysis and X-ray diffraction analysis were carried out to determine a suitable calcination temperature. The results indicate that a temperature above 1100 °C is required to eradicate the chloride ion. The powders yielded by spray drying were then calcined at 1150 °C for about 20 h and the resulting powders were characterized by X-ray diffraction using CuK_α radiation.

Fig. 6 shows the XRD pattern of $BaHfO_3$ from the spray drying. As can be seen from the figure, single phase of $BaHfO_3$ has been obtained and indexed.

4. Calculation of the upper bound on the volume percentage of the reacted powders by XRD analysis

XRD analysis was used to detect the possible reaction between YBCO and $BaXO_3$ (X = Zr, Hf). To calculate an upper bound on the approximate percentage of reacted volume, a simplified model was considered.

Suppose spherical particles, representing the starting powders of YBCO + $BaXO_3$, with a radius of R, are compacted by pressing. After reaction, if we assume a reaction layer of thickness t_0 all round the particle, the approximate volume ratio of the reacted products, V_t, and the unreacted material, V_u, can be calculated as

$$\begin{aligned} x &= V_t/V_u \\ &= \frac{4\pi R^2 t_0}{4\pi R^3/3} \\ &= 3t_0/R \end{aligned} \qquad (1)$$

If, conservatively, X-ray diffraction can detect $x > 5\%$ of new phase, then if no reaction is detected, the upper bound estimate for the thickness of the reaction layer is

$$t_0 < 0.013R \qquad (2)$$

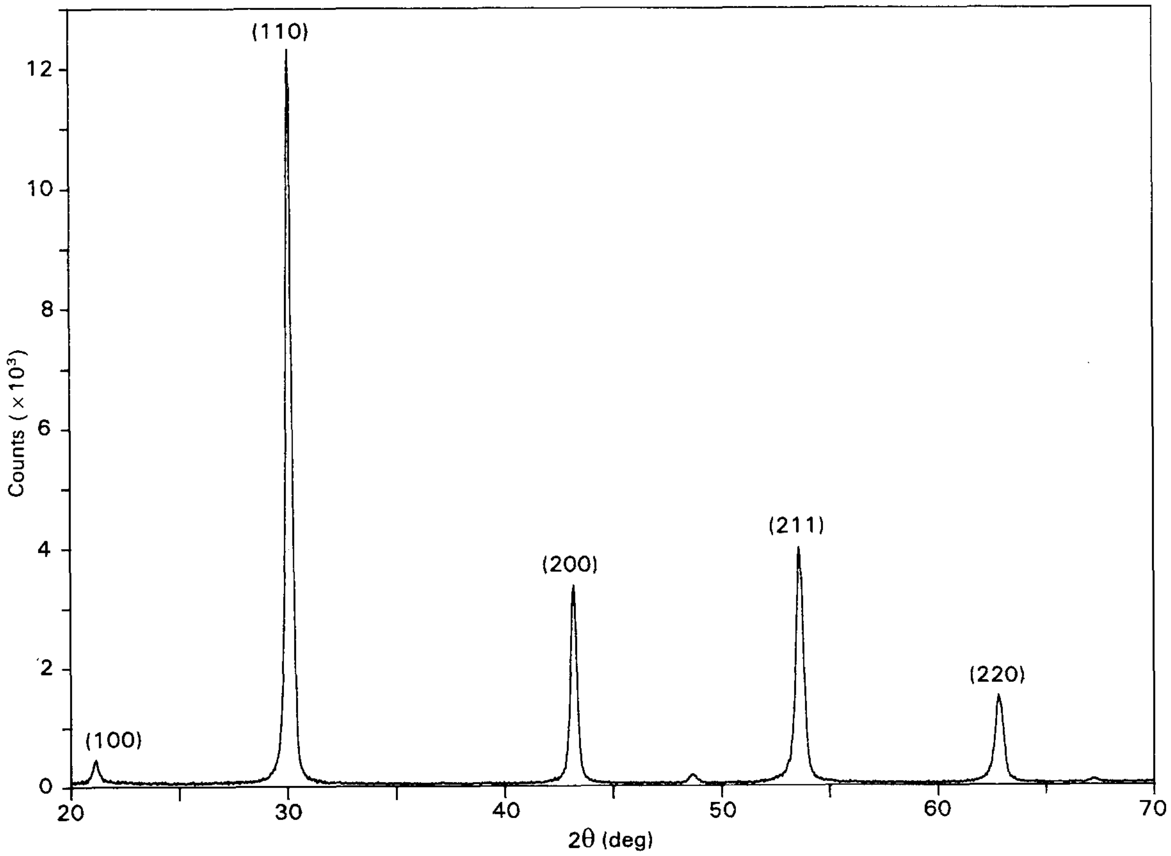

Figure 5 XRD pattern for $BaHfO_3$ (solid-state reaction).

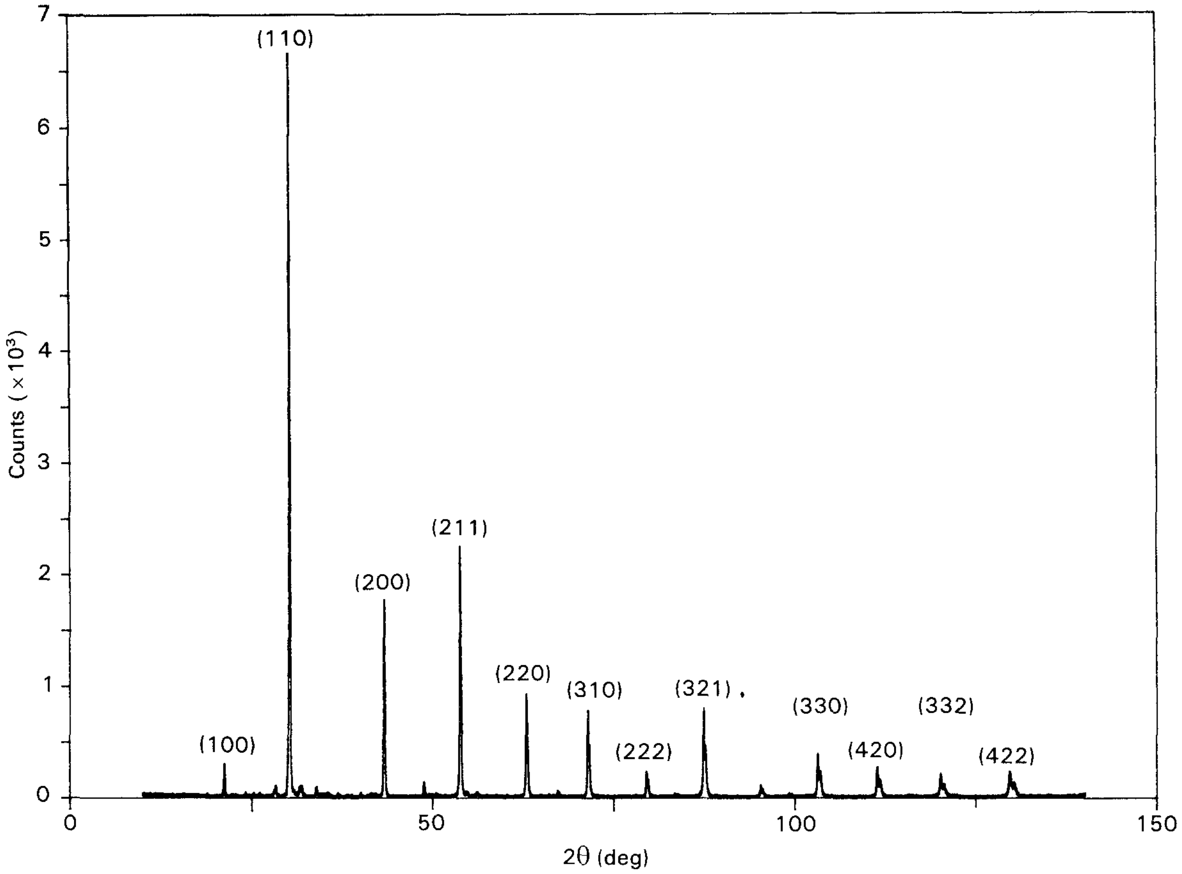

Figure 6 X-ray diffraction pattern for $BaHfO_3$ (spray-drying method).

5. The Interaction between YBCO and $BaZrO_3$

In order to increase the contact area between the reactants and the degree to which reaction can occur at a given temperature, a composite of mixed powders of YBCO (Hoechst, Germany) + $BaZrO_3$ was made to contain nominally 50 vol% YBCO with 50 vol% $BaZrO_3$. The powders (approximate mean size 5 μm) were mixed and heated at 950 °C for 5 h in air and cooled slowly in the furnace.

Fig. 7a shows the XRD pattern of YBCO + $BaZrO_3$ treated at 950 °C for 5 h. All reflection peaks could be indexed according to those expected for YBCO and $BaZrO_3$ in the figure. Because we do not detect new phase by XRD, we can deduce from Equation 2 that $t_0 < 0.013R < 65$ nm. This result indicates that no significant reaction occurs between YBCO and $BaZrO_3$ even after heat treatment at 950 °C for 5 h. In view of the fact that the maximum substrate temperature for the preparation of YBCO films is below 900 °C, it is suggested that $BaZrO_3$ is a very stable material for the deposition of superconducting films and for the fabrication of a container for bulk YBCO materials. However, the diffraction intensities (Fig. 7b) of YBCO in the YBCO + $BaZrO_3$ composite apparently decreases at 1000 °C for 5 h, which may suggest some reaction occurring at this temperature.

6. The interaction between YBCO and $BaHfO_3$

Composite YBCO + $BaHfO_3$ was fabricated to contain nominally 50 wt % YBCO with 50 wt % $BaHfO_3$ to increase the interfacial area between the reactant and, therefore, the degree to which reaction can occur at a given temperature. The powders were mixed and heated at 1000 °C for 10 h in air and cooled slowly in the furnace. The composite specimens were characterized by powder X-ray diffraction, using CuK_α radiation.

Fig. 8 shows the XRD pattern for YBCO + $BaHfO_3$ observed after 10 h at 1000 °C, and the lattice parameters for the two phases in the samples are compared with those of pure YBCO and $BaHfO_3$ samples. No new phase was found by XRD. Similarly, according to Equation 2, we can deduce that no significant reaction occurs. In addition, all reflections were indexed, based on those expected for YBCO and $BaHfO_3$ in the figure. This indicates that there was no solid solution between these two compounds, nor was a new phase obtained. These results confirm that there is no detectable reaction between YBCO and $BaHfO_3$ even after 10 h annealing at 1000 °C, with an upper bound estimate of the reaction layer $t_0 < 65$ nm.

In order to study the interaction of superconductors and a substrate by the melt-texture growth technique, the YBCO pellets were placed on the sintered $BaHfO_3$ substrates, inserted in a horizontal furnace and melt-textured according to the thermal cycle described below. The samples were heated up to 1060 °C for 5 min, quickly cooled to 1030 °C, then slowly cooled down to 930 °C at the rate of 4 °C h^{-1}. After that, they were cooled to 500 °C for 40 h, and then furnace cooled. The prepared samples were cut to observe the cross-section using optical microscopy, SEM and EDAX.

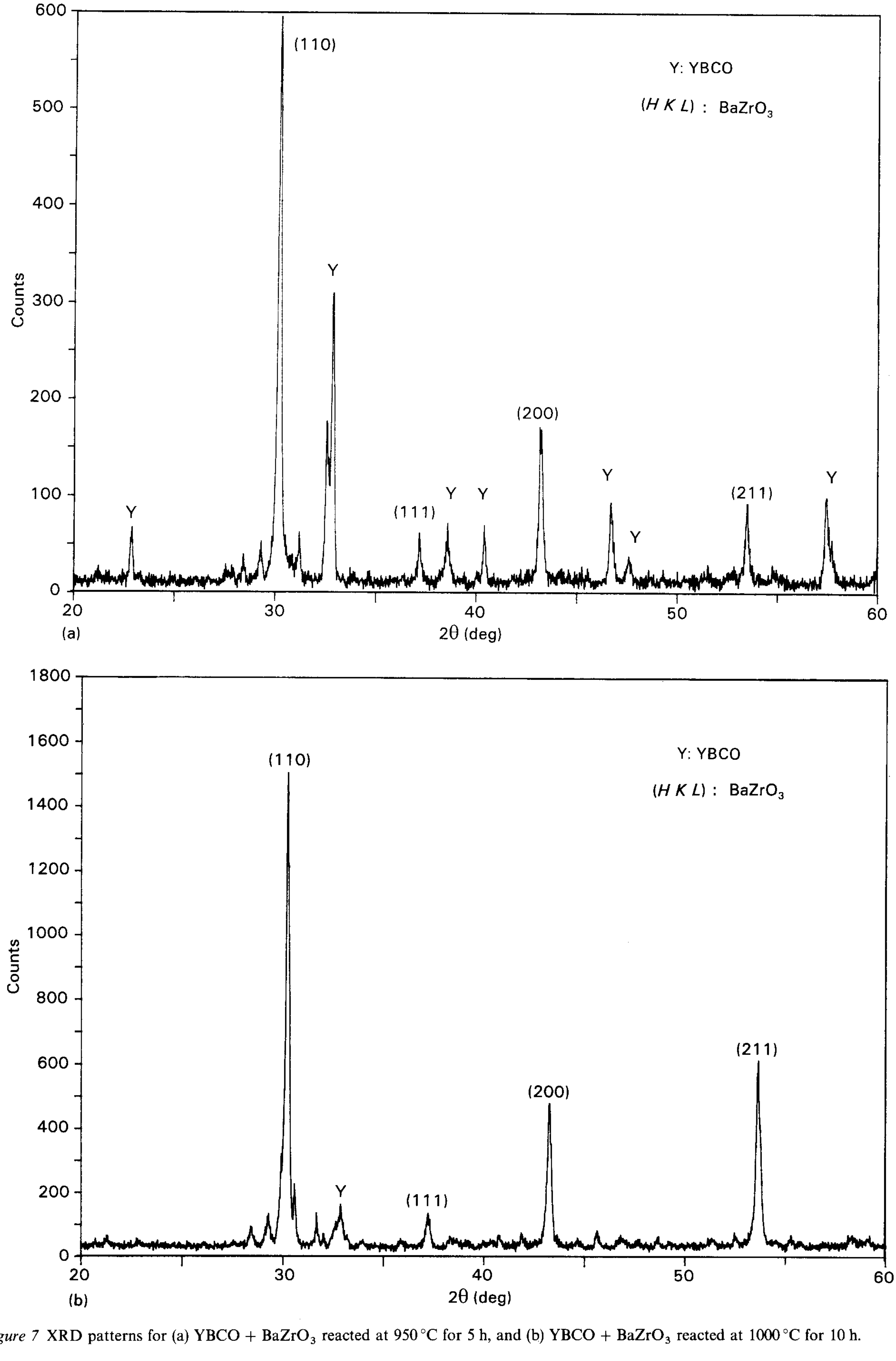

Figure 7 XRD patterns for (a) YBCO + BaZrO$_3$ reacted at 950 °C for 5 h, and (b) YBCO + BaZrO$_3$ reacted at 1000 °C for 10 h.

From the observation of the scanning electron micrograph of the interface between YBCO and BaHfO$_3$ after the melting-texture temperature cycle, the texture of YBCO is formed in the samples. The results of SEM and EDAX analysis indicate that although the melts from the YBCO pellet had percolated into the BaHfO$_3$ substrate material, no visible reaction between YBCO and BaHfO$_3$ had occurred. That suggests that BaHfO$_3$ is also a suitable substrate material for melting-texture technology.

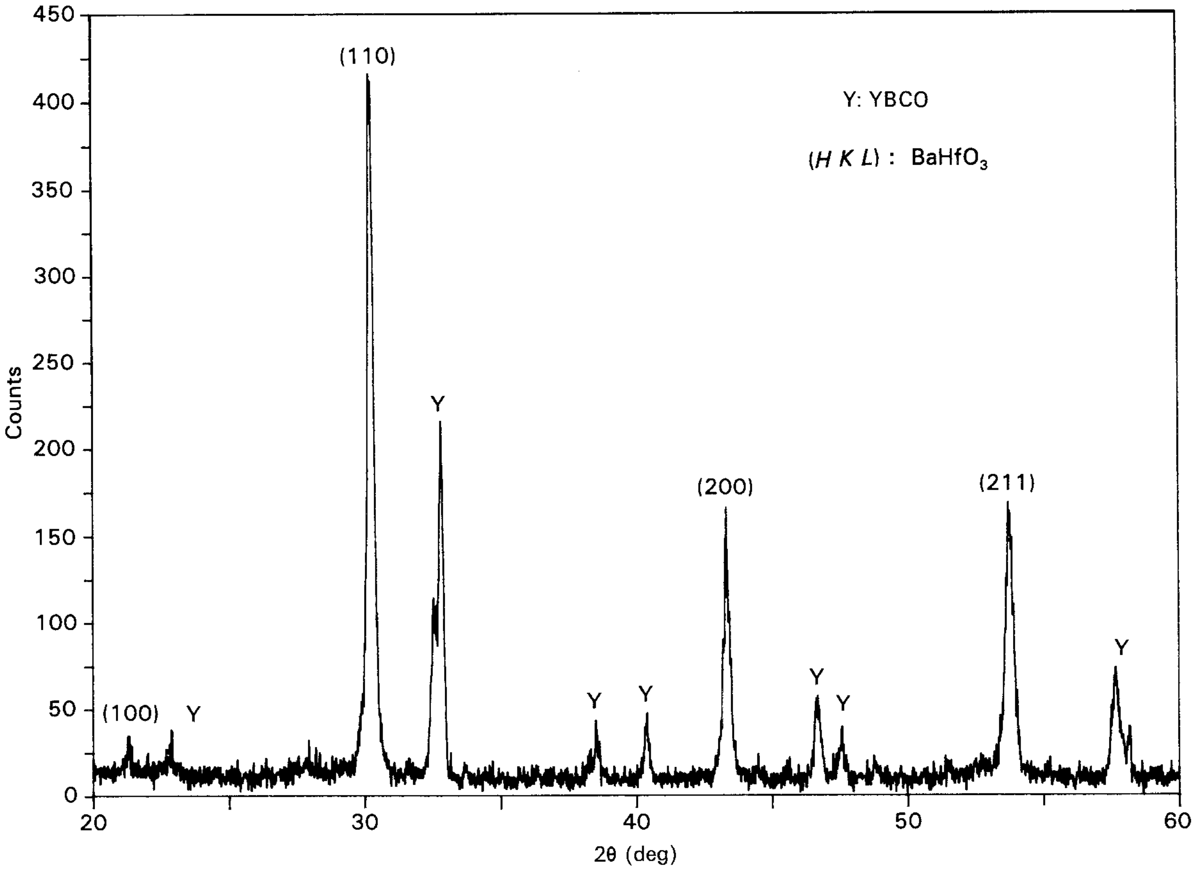

Figure 8 X-ray diffraction pattern for $BaHfO_3$ + YBCO reacted at 1000 °C for 10 h.

7. Conclusion

The reaction between $BaCO_3$ and HfO_2 to form $BaHfO_3$ occurs at about 990 °C. Single-phase $BaHfO_3$ can be synthesized at temperatures above 1040 °C, while sintered $BaHfO_3$ ceramics were obtained at 1300 °C for 24 h after calcination at 1040 °C for 4 h. Homogeneous powders of $BaZrO_3$ and $BaHfO_3$ can also be prepared by a spray-drying method.

Heat treatment of mixed YBCO + $BaZrO_3$ and YBCO + $BaHfO_3$ composites shows that no significant chemical reaction occurs between the components. No detectable reaction occurs between melts from YBCO and $BaHfO_3$ at temperatures below 1060 °C. In addition, both $BaZrO_3$ and $BaHfO_3$ possess a cubic perovskite type structure with a lattice constant of 0.4193 nm and 0.4171 nm. The lattice mismatch between $BaXO_3$ (X = Zr, Hf) and YBCO is smaller than that of MgO (fcc structure, $a = 0.4215$ nm) and YBCO. The results suggest that $BaZrO_3$ and $BaHfO_3$ are promising substrate materials and buffer layers for the fabrication of films and a good container for bulk YBCO materials. The comparison of the reaction YBCO + $BaHfO_3$ and YBCO + $BaZrO_3$ also indicates that $BaHfO_3$ could be a less reactive material than $BaZrO_3$.

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