

Characterization of ferroelectric and superconducting ceramics prepared from precursor carbonates

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Abstract. The advantages of a new semi-wet method for the synthesis of $(\text{Ba}, \text{Ca})\text{TiO}_3$ and $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$ powders from precursor carbonates are described. The precursor carbonates are prepared using chemical coprecipitation technique under controlled pH conditions to ensure uniform distribution of $\text{Ba}^{+2}/\text{Ca}^{+2}$ and $\text{Y}^{+3}/\text{Ba}^{+2}$ ions. It is shown that the powders synthesized by this route possess better chemical homogeneity as compared to those obtained by the conventional ceramic technique involving calcination of a mixture of BaCO_3 , CaCO_3 , TiO_2 and Y_2O_3 , BaCO_3 , CuO powders. The behaviour of the ferroelectric $(\text{Ba}, \text{Ca})\text{TiO}_3$ and the superconducting $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$ ceramics prepared from powders obtained by our method are found to be markedly different from those known for the conventionally prepared ceramics.

Keywords. Ferroelectric ceramics; superconducting ceramics; diffuse phase transition; ceramic powder processing; coherent domain size; line profile analysis.

1. Introduction

The physical properties of oxide ceramics are extremely sensitive to the procedure adopted for the synthesis of the starting powder material. The chemical homogeneity, crystallinity, particle size and reactivity of any powder are known to be influenced by the procedure used for its synthesis. In this work, we shall briefly describe a novel semi-wet route developed by us for the synthesis of ferroelectric $(\text{Ba}, \text{Ca})\text{TiO}_3$ and superconducting $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$ powders, and its influence on the ultimate physical behaviour of the ceramics prepared from these powders.

Amongst BaTiO_3 -based ceramics, the system $(\text{Ba}, \text{Ca})\text{TiO}_3$ has received considerable attention because of its improved electromechanical behaviour in transducer applications (Jaffe *et al* 1971). The room temperature structure of $\text{Ba}_{1-x}\text{Ca}_x\text{TiO}_3$ ($x \leq 0.21$) ceramics is tetragonal, with barium and calcium ions randomly occupying the A-site of the ABO_3 perovskite framework. Substitution of barium by calcium is known to increase the range of stability of the ferroelectric tetragonal phase to lower temperatures (Mitsui and Westphal 1961). Further, it inhibits the formation of the unwanted high temperature hexagonal phase of BaTiO_3 thereby facilitating higher firing temperatures leading to higher sintered density (Jaffe *et al* 1971).

The superconducting $\text{YBa}_2\text{Cu}_3\text{O}_7$ has also got the basic perovskite framework structure with oxygen deficiency (Cava *et al* 1987; Grant *et al* 1987; Rao *et al* 1987; Siegrist *et al* 1987). The crystal structure of this phase is orthorhombic with yttrium and barium ions occupying A-sites in an ordered fashion (Beno *et al* 1987; David *et al* 1987; Gallagher *et al* 1987; Hazen *et al* 1987) leading to tripling of the cell dimension

in the *c*-direction. The perovskite framework is stable for the oxygen content (*x*) in the range $6 < x < 7$, although for lower oxygen content the structure becomes tetragonal and loses superconductivity partially or completely (Tarascon *et al* 1987).

In the conventional method of preparation of $\text{Ba}_{1-x}\text{Ca}_x\text{TiO}_3$ powders via thermochemical reaction in a mixture of BaCO_3 , CaCO_3 and TiO_2 particles, uniform distribution of the A-site cations cannot be ensured at the atomic level even after repeated grinding and firing cycles. In fact, initial reaction will occur not only at the $\text{BaCO}_3\text{-TiO}_2\text{-CaCO}_3$ contact surfaces but also at $\text{BaCO}_3\text{-TiO}_2$ and $\text{CaCO}_3\text{-TiO}_2$ surfaces. Since the mixing is only at the particulate level, there will be regions with excess/deficient calcium concentrations. Uniform distribution of barium and calcium ions at the A-site will actually require very long diffusion distances of the order of a few tens of thousands of unit cells if the average reactant particle size is about a few microns. The microscopic chemical inhomogeneities resulting from the slow reaction kinetics due to the diffusional limitations are generally frozen-in and remain below the detection limit of the routine XRD technique employed for checking single phase formation. This problem can in principle be overcome if a precursor compound/solid solution containing all the cations in the desired stoichiometry could be synthesized using a wet technique. However it is not always possible to synthesize such precursors with desired stoichiometry. Further, with the increasing number of species to be coprecipitated for the precursor compound, control of pH becomes rather difficult.

In the technique developed by us to achieve mixing of the A-site cations on an atomic scale, we first prepare a solid solution of $\text{Ba}_{1-x}\text{Ca}_x\text{CO}_3$ using chemical coprecipitation (Pandey *et al* 1987). The precursor carbonate solid solution is then mixed with TiO_2 for thermochemical reaction to yield $\text{Ba}_{1-x}\text{Ca}_x\text{TiO}_3$. Thus the diffusional limitation of the conventional technique, where the initial reaction is rapid but further reaction gets increasingly slower as the product layer builds up and the diffusion distances become longer, is overcome since dissimilar atoms are statistically distributed at the unit cell level within each particle of the precursor carbonate solid solution. As compared to the typical separation of several tens of thousands of unit cells in the conventional mixture, in the solid solution precursor A-site cations are only a few unit cells apart irrespective of the size of the precursor particles. This ensures uniform supply of Ba^{+2} and Ca^{+2} in the correct ratio during solid state thermochemical reaction with TiO_2 particles. Thus the possibility of frozen-in compositional inhomogeneities, as also the unwanted phases, formed in response to local stoichiometric constraints, is drastically reduced. This method has the added advantage of continuously varying the A-site cation composition and is ideally suited for studying the effect of chemical substitutions in the ABO_3 structures if a suitable solid solution precursor can be formed.

Following the discovery of superconductivity above the boiling point of liquid nitrogen (Wu *et al* 1987) we applied our precursor technique to synthesize $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$ powders (Pandey *et al* 1988). However in this case the precursor is not a solid solution but instead an intimate mixture of very fine size barium carbonate particles (finer than the commercially available BaCO_3) and amorphous yttrium carbonate. Both the fine particle size and its amorphous nature enhance the reactivity of the precursor.

As a result of better compositional homogeneity, the physical behaviour of the ferroelectric $(\text{Ba}, \text{Ca})\text{TiO}_3$ and the superconducting $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$ ceramics prepared

from powders obtained by this method are found to be markedly different from those of the conventionally prepared ceramics. The purpose of the present work is to provide a brief overview of the work done by us on $(\text{Ba}, \text{Ca})\text{TiO}_3$ and $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$ ceramics prepared from powders obtained by the precursor route.

2. Synthesis of the precursor carbonate

The precursor carbonates were synthesized by adding ammonium carbonate solution to solutions of BaCl_2 mixed with CaCl_2 in one case, and YCl_3 in the second case, in the desired molar ratio. The filtrates in the two cases were checked for $\text{Ba}^{+2}/\text{Ca}^{+2}$, and $\text{Ba}^{+2}/\text{Y}^{+3}$, their absence confirming the complete coprecipitation of $\text{Ba}^{+2}/\text{Ca}^{+2}$ and $\text{Ba}^{+2}/\text{Y}^{+3}$ in the two types of precursors.

Figure 1 depicts the X-ray diffractometer record for the precursor prepared for the synthesis of $\text{Ba}_{0.90}\text{Ca}_{0.10}\text{TiO}_3$ powders. All the lines in this record can be indexed with respect to the orthorhombic structure of BaCO_3 with cell parameters $a = 5.17 \text{ \AA}$, $b = 8.93 \text{ \AA}$ and $c = 6.41 \text{ \AA}$. The absence of the most intense line of CaCO_3 at $2\theta = 29.403$ in figure 1 confirms that the calcium ions have indeed gone into the formation of a solid solution $\text{Ba}_{0.90}\text{Ca}_{0.10}\text{CO}_3$.

Figure 2a depicts the diffractometer record for the precursor prepared for synthesizing $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$ powders. In this case, the precursor may not be a solid solution of barium and yttrium carbonates. In fact, a comparison of the diffractometer records for pure BaCO_3 given in figure 2b with that for the precursor shows that there is no change in the peak positions within experimental errors. Since handbook data on yttrium carbonate is not available and the yttrium carbonate synthesized by us

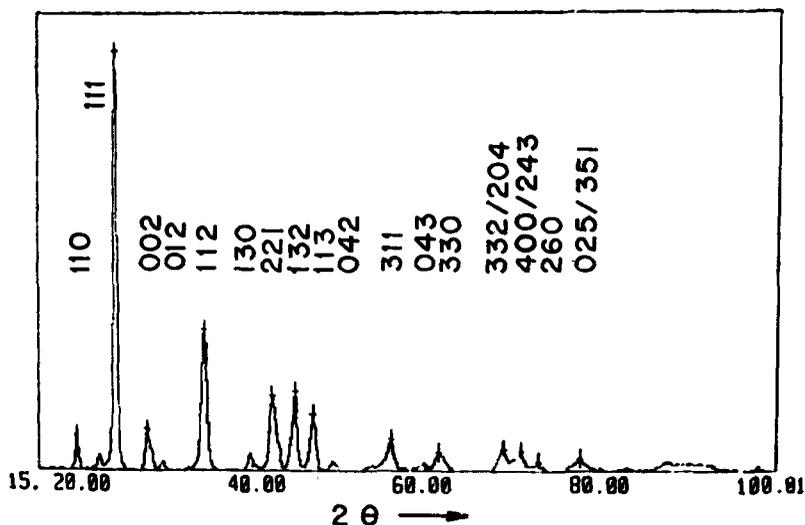


Figure 1. Powder diffractometer record of $\text{Ba}_{0.9}\text{Ca}_{0.1}\text{CO}_3$.

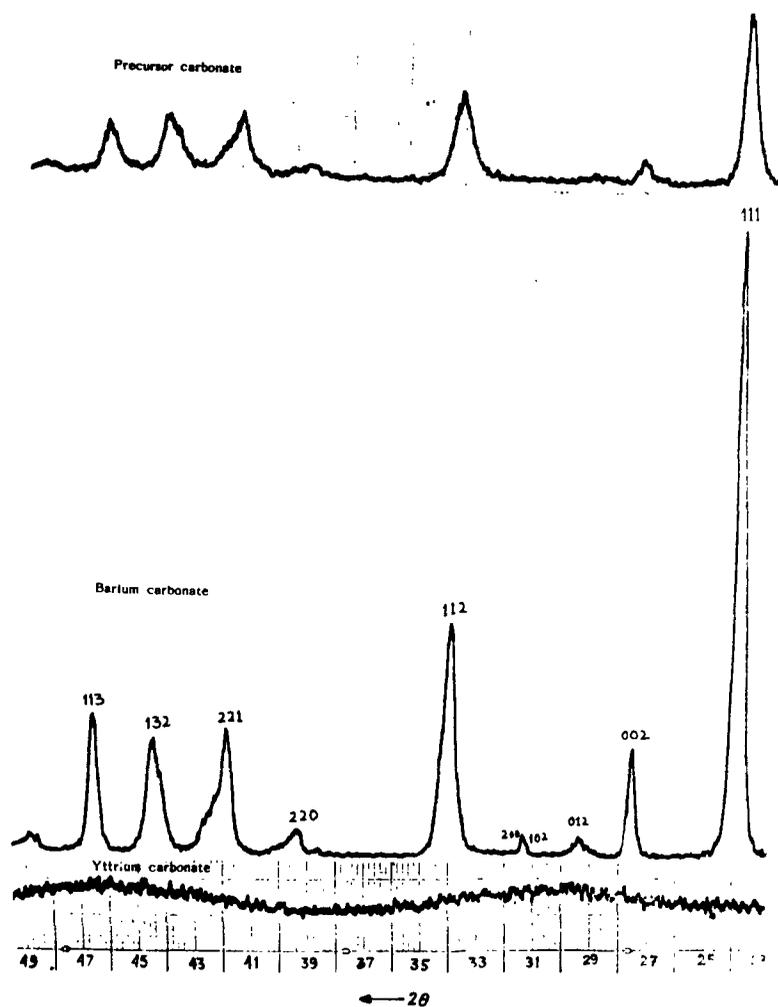


Figure 2. Powder diffractometer records of (a) precursor carbonate, (b) barium carbonate and (c) yttrium carbonate.

turned out to be amorphous (see figure 2c), it was not possible to decide from powder diffractometer records whether yttrium ions exist separately or have partially gone into the BaCO_3 matrix. In all probability, this precursor is an intimate mixture of very fine barium carbonate particles and amorphous yttrium carbonate. The fact that all the lines in the precursor are broader than those for the commercial BaCO_3 powder indicates that the barium carbonate particles in the precursor are finer in size than those in commercially available powders. Although no solid solution is formed in this case, finer barium carbonate particle size and the amorphous nature of the yttrium carbonate make the precursor chemically more reactive than an ordinary mixture of BaCO_3 and Y_2O_3 used in the conventional method for synthesizing $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$ powders.

3. Compositional homogeneity of powders prepared by the precursor and conventional routes

Powders of $\text{Ba}_{1-x}\text{Ca}_x\text{CO}_3$ and TiO_2 as well as BaCO_3 , CaCO_3 and TiO_2 were thoroughly mixed and subjected to two successive calcination runs of 12 and 6 h duration at 1150°C . The X-ray diffractometer records taken from these powders are given in figures 3a and b. As evident from figure 3, for the powder prepared by the

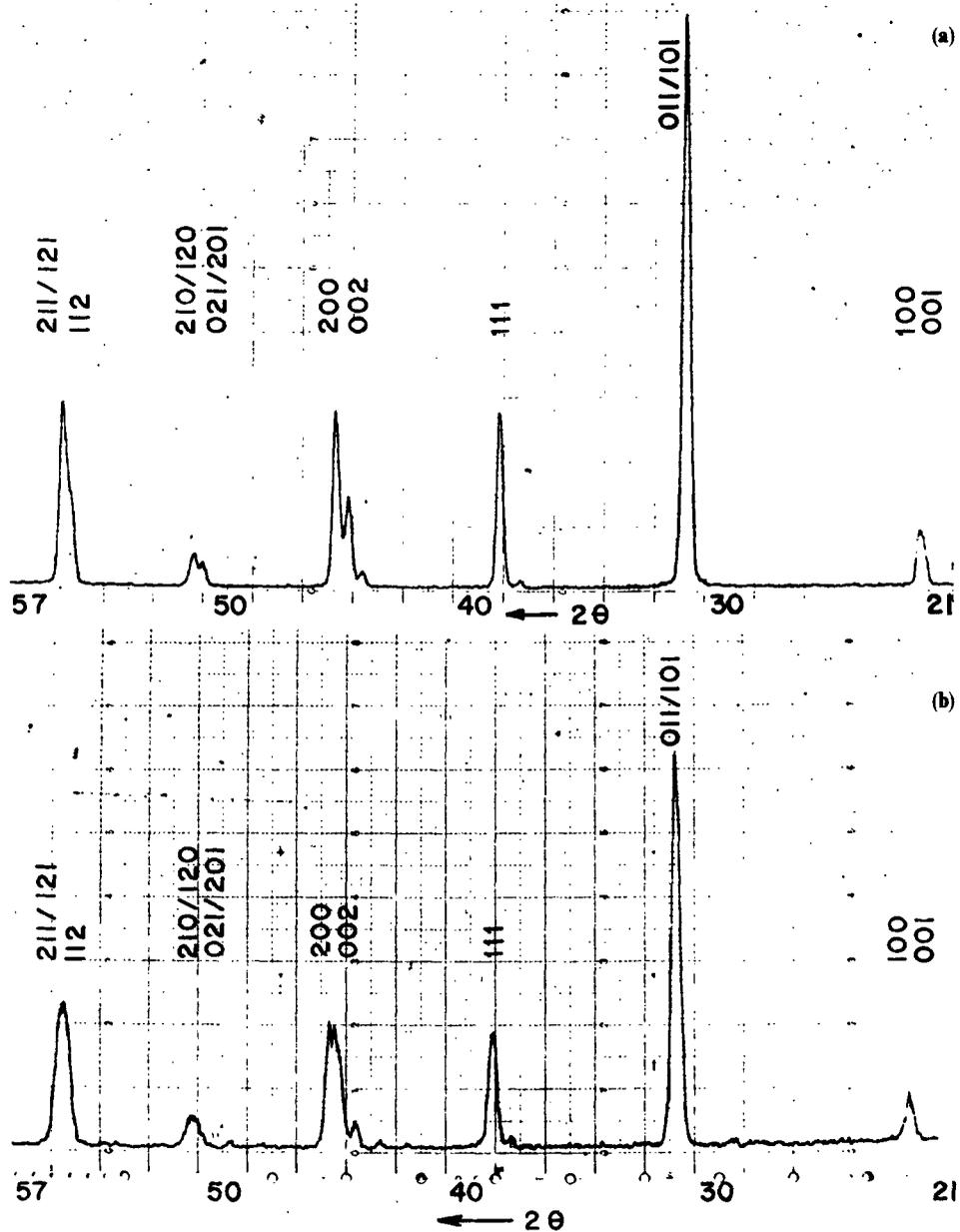


Figure 3. Powder diffractometer records of $\text{Ba}_{0.9}\text{Ca}_{0.1}\text{TiO}_3$ prepared by (a) solid solution precursor, and (b) conventional methods.

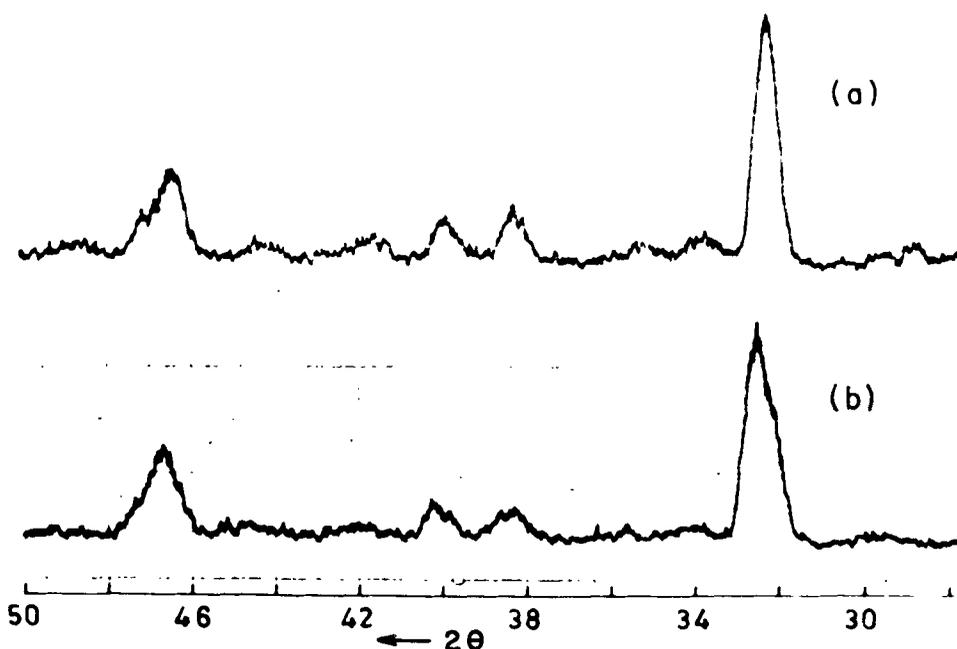


Figure 4. Powder diffractometer records of $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$, prepared by (a) precursor and (b) conventional routes.

precursor route the 200 and 002 peaks of the tetragonal phase are very sharp and well-resolved. The observed broadening of various reflections for the conventionally prepared powders is not due to smaller particle size, since the powder particles obtained by the conventional route are coarser than those obtained by the precursor route. The observed broadening of reflections in figure 3b has thus to be attributed to fluctuations in d spacings due to compositional inhomogeneities. As shown elsewhere using structure factor calculations (Tiwari *et al* 1989), calcium ions replace barium ions at A-sites in compounds prepared by the precursor route only.

Figures 4a and b depict the diffractometer records for $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$ powders synthesized by the precursor and conventional routes, respectively. In both cases, the constituent powders were calcined at 900°C twice, each time for a duration of 12 h. Even after the two calcination cycles, the powders are not truly single phase but become so after sintering of the pellets (prepared at a pressure of 57,000 psi) in flowing oxygen at 900°C for 6 h followed by furnace cooling. The diffractometer records in figure 4 are from powders obtained by crushing the pellets prepared by the two routes. As in the case of $\text{Ba}_{1-x}\text{Ca}_x\text{TiO}_3$, the observed broadening of various reflections for the conventionally prepared powder is due to compositional inhomogeneities and not due to smaller particle size since the powder particles obtained by the conventional route are coarser than those prepared by the precursor route.

The patterns given in figures 4a and b are for pellets which were furnace-cooled. As a result of this, the orthorhombic splitting has not come out clearly in these patterns. The only clue to the structure being orthorhombic is provided by the higher intensity of the 006 and 020 lines as compared to that of the 200 near $2\theta = 46.5$ and $2\theta = 47.0$ respectively. However, if the pellet is cooled slowly in flowing oxygen, we get the

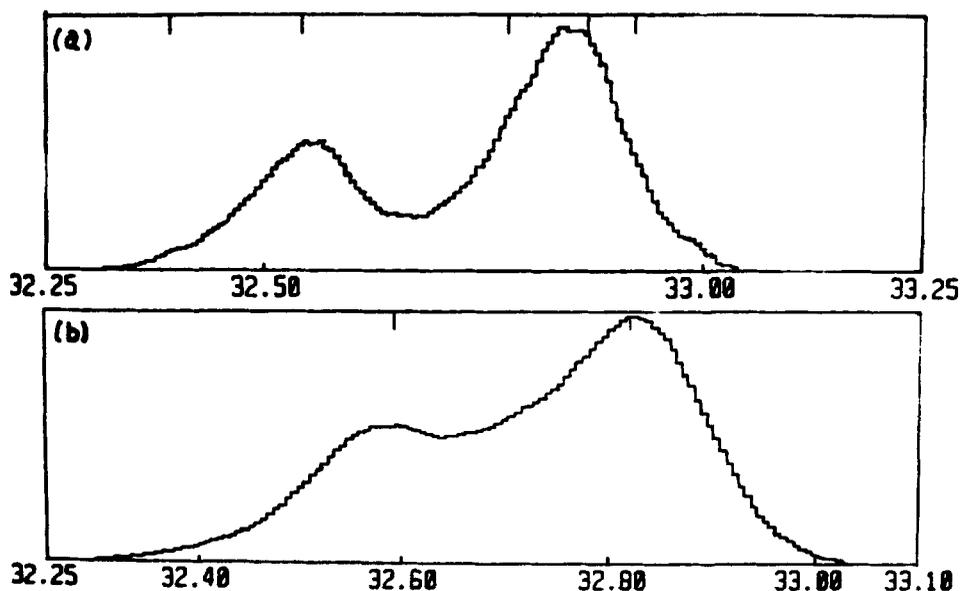


Figure 5. XRD lines of $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$ near $2\theta = 32^\circ$ for the samples prepared by (a) precursor and (b) conventional routes.

Table 1. Cell parameters of $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$ prepared by the precursor and conventional routes.

Sample type	a (Å)	b (Å)	c (Å)
Precursor, furnace-cooled	3.848	3.870	11.720
Conventional, furnace-cooled	3.836	3.886	11.755
Precursor, slowly cooled	3.818	3.887	11.669
Conventional, slowly cooled	3.826	3.888	11.660

typical splitting of lines near $2\theta = 32^\circ$, 38° and 46° as shown in figures 5a and b for the lines near $2\theta = 32^\circ$ for specimens prepared using precursor and conventional routes respectively. Once again, the lines in figure 5a are sharper than those in figure 5b indicating better compositional homogeneity achievable by the precursor route.

The calculated cell parameters for patterns given in figures 4 and 5 are given in table 1. It is possible to quantify the level of compositional inhomogeneity using the principles of line profile analysis (Tiwari *et al* 1988; Pandey *et al* 1989). Compositional inhomogeneity in the powder specimens will lead to fluctuations in d spacings. As a result of this, the diffraction profile will be broadened and its halfwidth (β) will be given by

$$\beta(\theta) = (\Delta d/d) \tan \theta$$

There may be broadening due to the fineness (small size) of the particles also. The halfwidth of a diffraction profile for small particles is given by the well-known Scherrer equation

$$\beta(\theta) = \lambda/(\bar{D} \cos \theta).$$

Here, λ is the wavelength and \bar{D} is the average coherent scattering domain size. Thus in a plot of $\beta \cos \theta$ versus $\sin \theta$, the slope of the straight line gives $\Delta d/d$ due to compositional inhomogeneities whereas its intercept at $\sin \theta = 0$ yields the particle size broadening.

Figures 6 and 7 depict the $\beta \cos \theta$ vs $\sin \theta$ plots for $\text{Ba}_{0.88}\text{Ca}_{0.12}\text{TiO}_3$ and $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$ powders (obtained from slowly cooled specimens) prepared by the

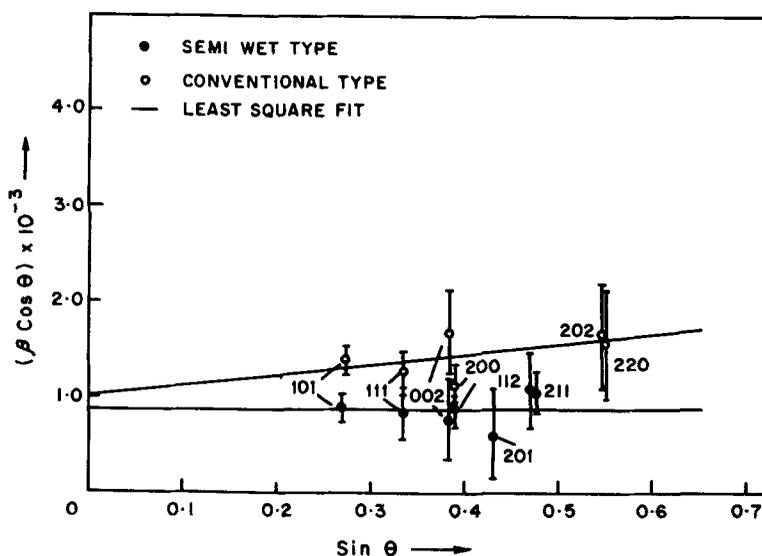


Figure 6. Variation of $\beta \cos \theta$ as a function of $\sin \theta$ for $\text{Ba}_{0.88}\text{Ca}_{0.12}\text{TiO}_3$ prepared by conventional and solid solution precursor methods (after Tiwari and Pandey, to be published).

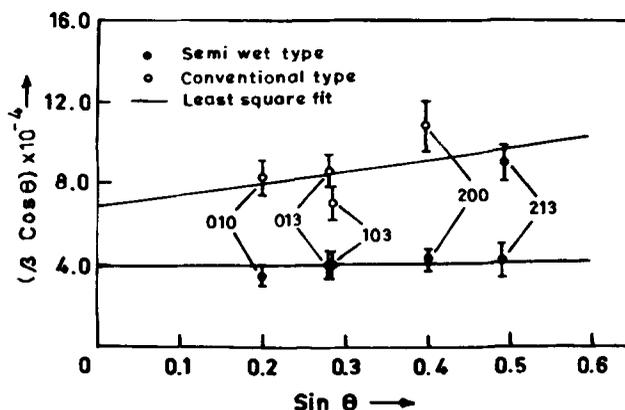


Figure 7. Variation of $\beta \cos \theta$ as a function of $\sin \theta$ for $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$ prepared by conventional and precursor routes (after Tiwari et al 1988).

two routes. It is evident from these figures that $\beta \cos \theta$ corresponding to samples prepared by the precursor/semi-wet route does not show any $\sin \theta$ dependence. Thus the precursor method yields powders free from compositional inhomogeneities. On the otherhand, samples prepared by the conventional route under identical conditions contain compositional inhomogeneities. The scanning electron micrographs of fractured ceramic pellets of $\text{Ba}_{0.88}\text{Ca}_{0.12}\text{TiO}_3$ prepared by conventional and solid solution precursor method show average grain sizes of about 5 and 1 μm respectively. The superconducting ceramic samples prepared by both the routes show an average grain size of about 5 μm . The coherent scattering domain sizes calculated from figures 6 and 7 for $\text{Ba}_{0.88}\text{Ca}_{0.12}\text{TiO}_3$ and $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$ prepared from both the routes are smaller than 1 μm . In the process of crushing these pellets, particle sizes smaller than one micron are not expected. Therefore, it can be concluded that the coherent scattering domain size is not the particle size of $\text{Ba}_{0.88}\text{Ca}_{0.12}\text{TiO}_3$ and $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$ specimens. As explained later, particles of both materials contain twin boundaries which seem to restrict the size of the coherent scattering domains.

4. Diffuse phase transition in (Ba, Ca)TiO₃ ceramics

The temperature-dependence of the dielectric constants of $\text{Ba}_{1-x}\text{Ca}_x\text{TiO}_3$ ceramics has been studied in detail by Mitsui and Westphal (1961) who prepared these ceramics from preformed BaTiO_3 and CaTiO_3 powders. It is found that ceramics, prepared using Mitsui and Westphal's procedure or the conventional route described in the previous section, exhibit sharp ferroelectric–paraelectric phase transitions. On the other hand, ceramics prepared by the precursor route show broadening of the dielectric constant vs. temperature curve indicating that the ferroelectric–paraelectric phase transition is taking place over a wide range of temperatures (Tiwari 1985; Pandey *et al* 1987). Ferroelectric materials exhibiting such diffuse phase transitions (DPT) have attracted considerable attention in recent years because of new physical phenomenon observed in them (see Newnham and Cross 1981). One of the main characteristics of DPT materials is the pronounced frequency dependence of the dielectric constant and loss even at low frequencies (kHz); in particular, dielectric loss is found to increase with increasing frequency while the dielectric constant decreases. In these materials, the temperatures at which the dielectric constant and loss attain the maximum value do not coincide and shift to the higher side with increasing frequency (Walter and Burggraaf 1975; Smolensky 1970; Kirillov and Isupov 1973). While the ferroelectric–paraelectric transition in (Ba, Ca)TiO₃ ceramics prepared by the precursor route is diffuse, there is no evidence for any kind of shift to higher temperatures in the peak value of dielectric constant and loss with increasing frequencies up to MHz. Further, the dielectric loss is found to decrease with increasing frequency whereas the dielectric constant does not change significantly. Figures 8a and b depict the temperature dependence of the real (ϵ') and imaginary (ϵ'') parts of the dielectric constant for a $\text{Ba}_{0.90}\text{Ca}_{0.10}\text{TiO}_3$ specimen prepared by the precursor route.

As pointed out by Pandey *et al* (1987), the DPT behaviour of the (Ba, Ca)TiO₃ ceramics cannot be explained in terms of the existing theories based on smallness of the grain size or compositional inhomogeneities but has to be attributed to the intrinsic structural disorder. In structurally disordered systems, the internal field will be

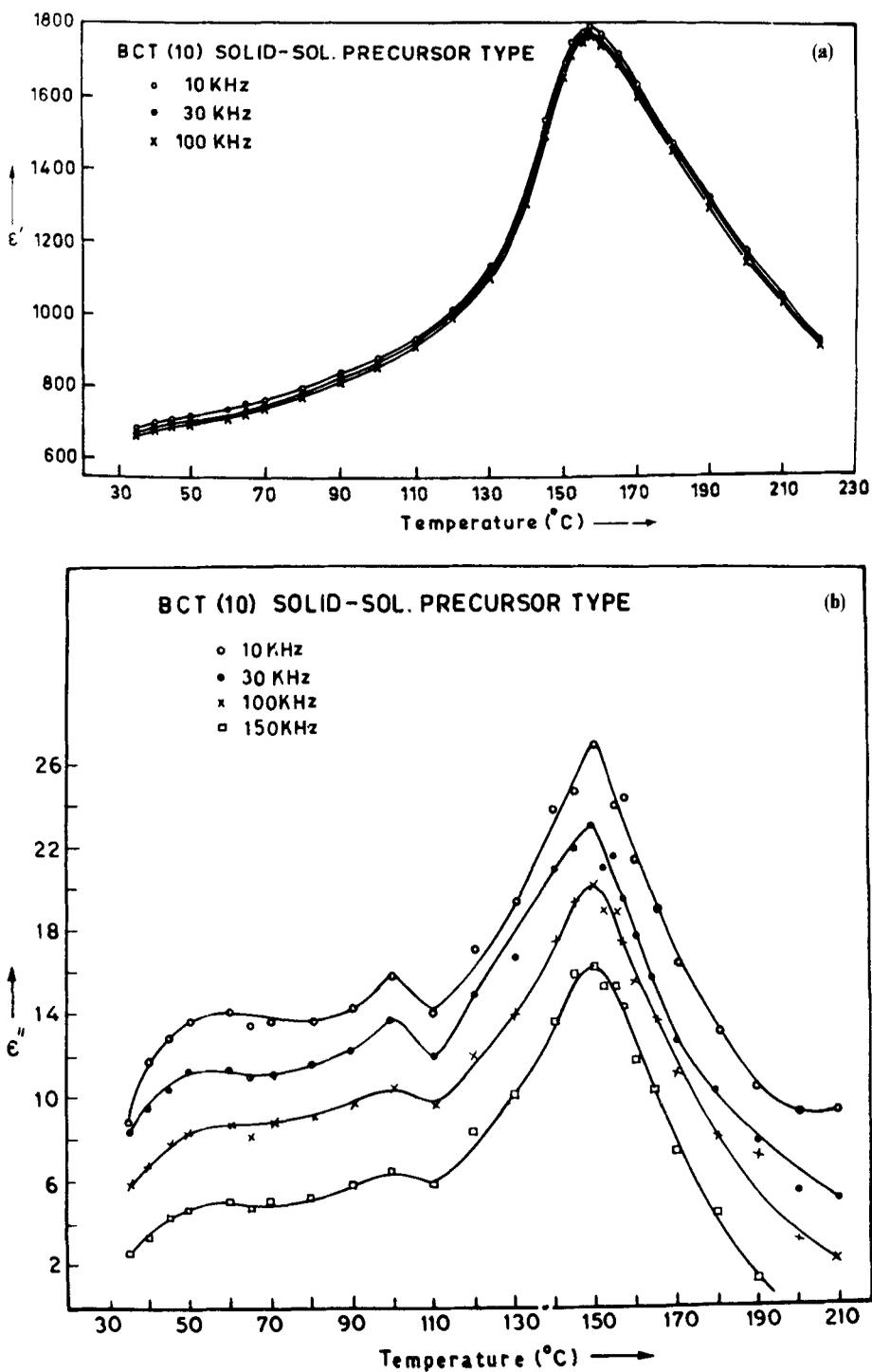


Figure 8. Frequency dependence of (a) ϵ' and (b) ϵ'' versus temperature-curve for the $\text{Ba}_{0.9}\text{Ca}_{0.1}\text{TiO}_3$ ceramic prepared by the solid solution precursor method (after Tiwari *et al* 1989).

perturbed irregularly due to the compositional fluctuations at the unit cell level. As a result, the cancellation of short range elastic forces by long range coulombic forces will occur at different temperatures in different microregions of the specimen. Thus the observed dielectric constant versus temperature curve will be a broad envelope of the local phenomena taking place in these microregions. Since the perturbation due to the substituting ion will depend on its random occupancy as well as the difference in size and valence relative to the matrix ion, mixed perovskites may exhibit DPT behaviour to varying extents. In systems where cations occupying the same lattice site undergo order-disorder transition, the phase transition becomes sharp for the ordered configuration (Setter and Cross 1980; Groves 1985; Stenger and Burggraaf 1980a, b). This clearly demonstrates the role of structural disorder in the DPT behaviour.

The distribution of barium and calcium ions in the conventionally prepared specimens can be made more homogeneous by resorting to an increasing number of calcination cycles. We have shown that with increasing numbers of calcination cycles, conventionally prepared specimens gradually approach the DPT behaviour exhibited by the ceramics prepared by the precursor route (Tiwari *et al* 1989). Thus homogenisation of the structural disorder leads to more pronounced diffuse transition with the dielectric loss decreasing with increasing frequency. It is likely that some of the dielectric relaxation observed in the conventionally prepared ceramics is due to the interfacial polarizabilities resulting from compositional inhomogeneities within the specimen.

5. Superconducting behaviour of $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$ ceramics

The superconducting behaviour of conventionally prepared $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$ and other rare earth cuprates has been studied extensively. The superconducting transition temperature is found to be extremely sensitive to the oxygen content. $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$ ceramics with $y = 0.1$ show superconductivity in the vicinity of 90 K (Murphy *et al* 1987; Hor *et al* 1987). With decreasing oxygen content, T_c goes down drastically and finally superconductivity disappears at $y = 0.6$ (Tarascon *et al* 1987). It is generally believed that the integrity of Cu–O chains parallel to the b-axis of the orthorhombic structure in the copper–oxygen plane containing no other oxygen atoms is crucial for high temperature superconductivity. With the knocking-off of oxygen atoms from these chains, T_c goes down and the structure eventually becomes tetragonal for $y \leq 0.60$.

Figure 9 depicts the temperature dependence of normalized resistivity for a specimen prepared by our precursor route showing a very sharp drop in resistivity near 110 K with a $T_c^{R=0}$ of 94 K. Contrary to the usual linear temperature dependence of resistivity from room temperature down to T_c^{onset} for the conventionally prepared specimens (Benoit *et al* 1987; Cava *et al* 1987; Iwazumi *et al* 1987; Murphy *et al* 1987; Tarascon *et al* 1987; Wu *et al* 1987), there is a kink at P near 260 K in figure 9. This kink is not followed at lower temperatures by an exactly linear resistance drop up to Q. Indeed there are oscillatory trends in the region PQ, and the slopes at P and Q (shown by dotted lines in the figure) do not match. In view of the foregoing, one may be tempted to propose that isolated superconducting regions start appearing below 260 K but the percolative superconducting path involving a reasonable fraction

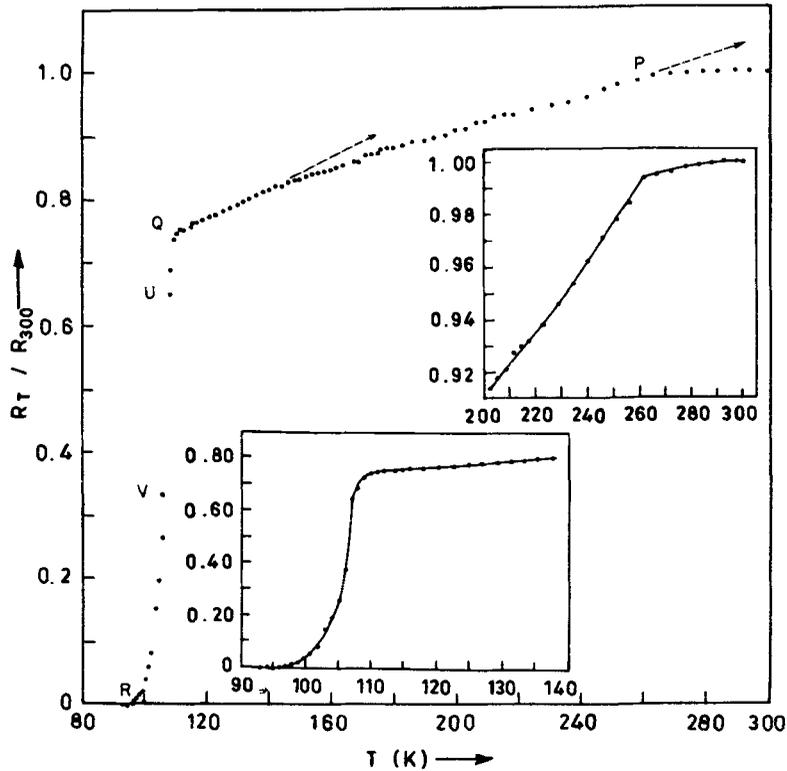


Figure 9. Temperature dependence of normalized electrical resistance (R_T/R_{300}) for $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$ ceramic prepared by the precursor route (after Pandey *et al* 1988).

of the entire specimen is established only below 110 K. The small increase in slope in going from P to Q can then be taken to represent a gradual increase in the fraction of superconducting regions. While it is now known that T_c^{onset} is definitely not 260 K, the observation was the first of its kind in the single phase $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$ at the time of its discovery in August 1987 (Pandey *et al* 1988). The possibility of some other phase responsible for this 260 K anomaly can not be ruled out especially if its volume fraction is below the detection limit of routine X-ray diffraction. It should be noted that Jayaram *et al* (1987) also reported anomalies above 230 K but in multiphase specimens where the phase responsible for the anomaly is yet to be identified. Chen *et al* (1987) reported weak superconducting signals through an inverse AC Josephson effect up to 240 K in $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$. There are now of course other reports suggesting that something unusual is happening around 240 K (Bhargava *et al* 1987).

Figure 10 depicts the temperature dependence of low field AC susceptibility (χ') on a powder specimen prepared by the precursor route. As is evident from the curve, the superconducting paths appear only at 92.8 K. The diamagnetic shift increases rapidly with further cooling below this temperature. The curve shows a sharp fall in magnetic susceptibility even in powder specimens with T_c^{midpoint} at 90.9 K. Usually the transitions are found to be sharper in pellets than in powders (Grover *et al* 1988). The 25–75% and 10–90% transition widths are found to be 2.8 and 8.2 K respectively. Although the susceptibility results appear to be at variance with the resistivity measurements,

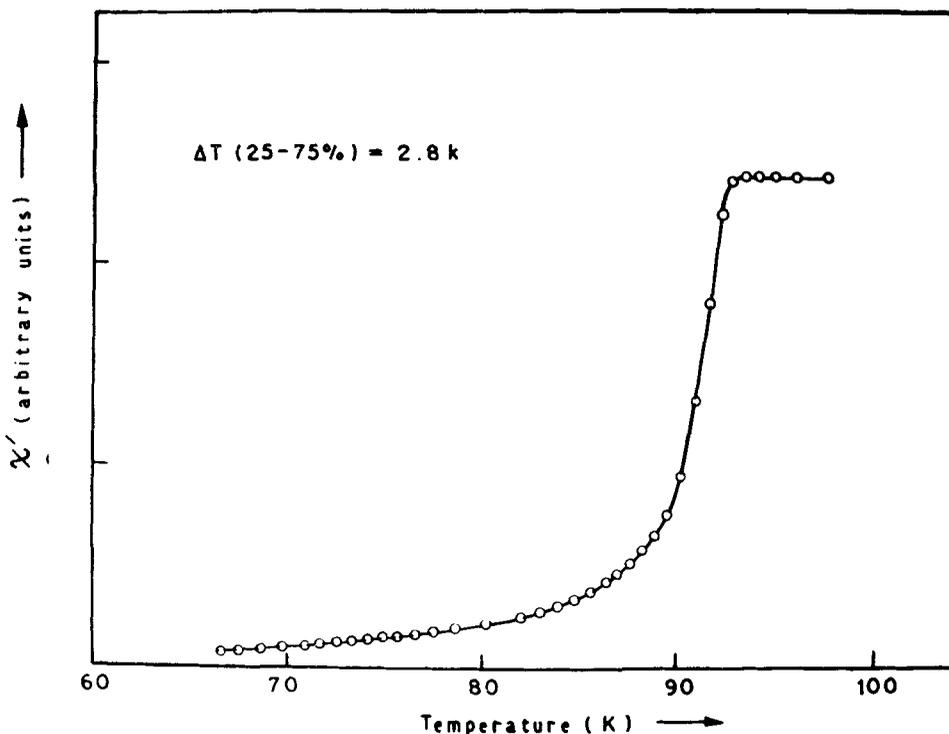


Figure 10. Temperature dependence of AC susceptibility (χ') of $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$ powder prepared by the precursor route.

where we found an abrupt fall in resistivity just below 110 K, the sharpness of the χ' versus T curve shows that the samples prepared by the precursor route have a higher volume fraction of the superconducting phase. Further, the closeness of $T_c^{R=0}$ of 94 K (see figure 9) and the onset temperature of 92.8 K for diamagnetic response is not easily achievable in specimens prepared by the conventional route. In fact, the two temperatures for conventionally prepared specimens usually differ by 5 to 10 K depending on processing conditions.

One of the factors which might be responsible for the improved superconducting behaviour of $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$ specimens prepared by the precursor route is higher chemical purity. In order to check this, we performed EDX analyses of specimens prepared by the conventional and precursor routes. Calcium was found to be the dominant impurity element followed by Al and Si in the conventionally prepared specimens (see figures 11a and b). In fact a few very small grains had predominantly calcium as shown in figure 11b. The majority of the grains were of course pure, and a typical EDX pattern is shown in figure 11c. On the other hand, specimens prepared by the precursor route did not show any evidence for the presence of calcium. A typical EDX pattern for such a specimen is given in figure 11d. Since the replacement of barium by calcium in general lowers T_c (Murphy *et al* 1987), the absence of calcium as impurity in specimens prepared by the precursor route might be one of the factors responsible for improved superconducting transition temperatures.

In addition to the absence of impurity elements, the specimens prepared by the precursor route are free from compositional inhomogeneities as already discussed in

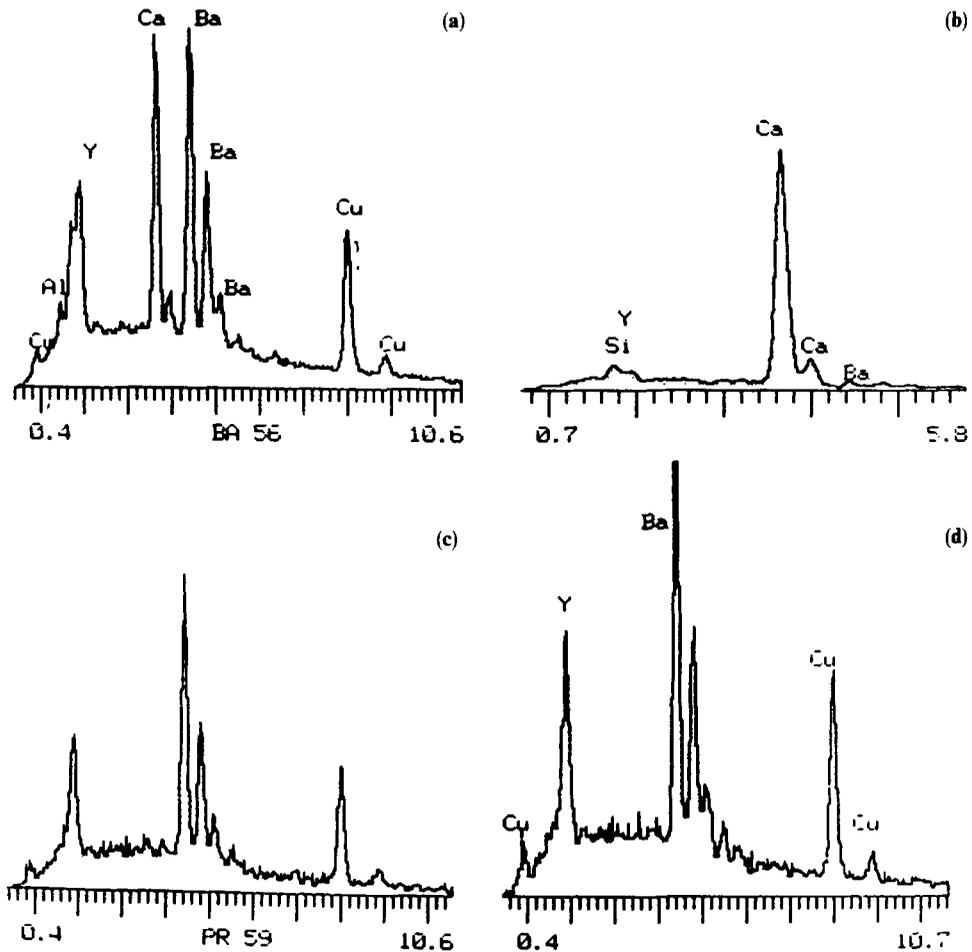


Figure 11. EDX analysis on different grains of conventionally prepared $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$ ceramic showing (a) calcium as dominant impurity, (b) presence of only Ca, Y, Si and Ba and (c) without any impurity atom. (d) EDX analysis of a typical grain of $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$, prepared by the precursor route.

§3. The average coherent scattering domain size, calculated from $\beta \cos \theta$ at $\sin \theta = 0$, is smaller in the case of powders prepared by the conventional method ($\sim 2200 \text{ \AA}$) than that of powders prepared by the precursor route ($\sim 4000 \text{ \AA}$). Since fundamental reflections hkl with $l = 3N$ were used in the line profile analyses, the coherent scattering domain size cannot represent the size of the ordered Y/Ba regions. The only other possible reason for the existence of domains within each particle is the presence of twin interfaces. It is now well-known that twins are formed during tetragonal to orthorhombic phase transition taking place as a function of oxygen content. Thus we can conclude that the specimens prepared by the precursor route have a lower density of twin boundaries than that for samples prepared by the conventional route. In order to correlate superconductivity with compositional inhomogeneities and the concentration of twin interfaces within each superconducting grain, we prepared $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$ ceramics under identical conditions (sintering temperature 900°C)

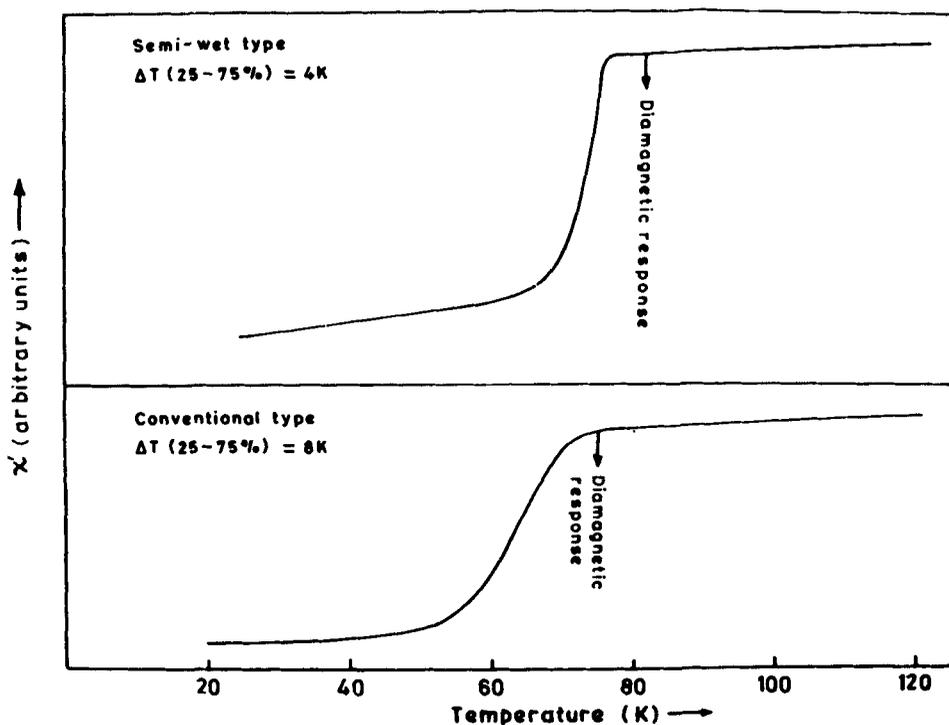


Figure 12. Temperature dependence of AC susceptibility of $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$ ceramics prepared by (a) precursor and (b) conventional routes.

using powders obtained by the conventional and precursor routes. Figures 12a and b depict the diamagnetic response for the two sets of specimens in ceramic form. It is worth mentioning that the precursor carbonate used in this case was prepared by adding ammonium carbonate solution drop by drop to a solution of YCl_3 and BaCl_2 and maintaining the pH between 6.0 and 8.0. The precursor used in the preparation of ceramics, whose χ vs. T behaviour is shown in figure 9, was synthesized by spontaneous precipitation on adding a large quantity of ammonium carbonate solution at a time to the solution of YCl_3 and BaCl_2 . The difference in the synthesis procedure for the precursor seems to influence T_c considerably (compare figures 10 and 12a). It is evident from figures 12a and b that the transition in the specimens prepared by the precursor route is sharper ($\Delta T_{25-75\%} \approx 4\text{ K}$) than that in the conventionally prepared specimens ($\Delta T_{25-75\%} \approx 8\text{ K}$). This clearly demonstrates the detrimental role of the compositional inhomogeneities and the higher concentration of twin interfaces on the superconducting behaviour of $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$ ceramics. More work on this line is currently in progress in our laboratory.

6. Conclusion

Use of precursor carbonates synthesized by a wet-technique can drastically affect the ferroelectric and superconducting behaviour of $(\text{Ba}, \text{Ca})\text{TiO}_3$ and $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$ ceramics. Contrary to the existing belief that compositional inhomogeneities might

be responsible for diffuse phase transitions in complex ferroelectric ceramics, we have shown that better chemical homogeneity indeed leads to diffuse phase transition. In $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$ ceramics, the precursor route has the potential of increasing the volume fraction of the superconducting regions. We have demonstrated the detrimental role of compositional inhomogeneities and twin interfaces on the high T_c superconductivity of $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$.

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