

Synthesis of $\text{YBa}_2\text{Cu}_3\text{O}_7$ through different gel routes *

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Abstract

High temperature superconducting $\text{YBa}_2\text{Cu}_3\text{O}_7$ (123) compounds were synthesized through various sol-gel processes using acetate, nitrate-citrate, acetate-citrate and acrylamide gel routes. The gel samples were characterized using IR, electronic and electron spin resonance (ESR) spectroscopy and scanning electron microscopy and the bonding behaviour in the gels was established and correlated to the phase purity of the 123 compound. Heat-treated gel samples were characterized by X-ray diffraction and superconducting properties were evaluated by resistivity and susceptibility measurements. IR, electronic and ESR spectral studies indicated that gels derived from acetate and acetate-citrate routes contained isolated copper acetate groups, whereas homogeneous heterometal ionic networks were observed in gels derived from nitrate-citrate. The ESR spectrum of acrylamide gels suggested homogeneous distribution of the copper(II) ions in the acrylamide polymeric network giving clearly resolved parallel and perpendicular features characteristic of copper(II). The samples derived from the acrylamide gel route are found to yield single-phase 123 compound with sharp resistive and diamagnetic transitions at 90 K, whereas other gel routes yielded multiphase samples with impurities of either BaCuO_2 or Y_2BaCuO_5 phases.

Keywords: Gel routes; Synthesis; Copper; Barium; Yttrium

1. Introduction

A large number of synthetic routes for the preparation of $\text{YBa}_2\text{Cu}_3\text{O}_7$ (123) superconducting oxides are reported in the literature. The normal state and superconducting properties of polycrystalline 123 materials depend on the microstructure which is in turn determined by the preparative methods. The most common method of synthesis is the classical ceramic route [1,2] using metal oxides as starting materials. The inherent drawbacks associated with the ceramic route of synthesis, i.e. inhomogeneity in the mixing of the starting materials, slow reaction rates etc., make it difficult to obtain fine and homogeneous powders of 123. In order to improve the homogeneity and to obtain higher yields of the superconducting phase, repeated grindings and calcination over extensive periods are recommended and practised in solid state reactions [2]. However, better homogeneity and purity of the material are achieved through sol-gel processes via citrate [3,4], alkoxide [5,6], acetate [7,8] and acrylamide [9] routes. A close control

over microstructure of the final product is also achieved [8] by varying the initial process conditions and changing the complexing ion in the solution. The gel route is thus established as a process through which fine particles and homogeneous powders can be produced [10].

Since the quality assurance of the final product is dependent on the homogeneity and the bonding behaviour of the metal complexes within the gel, a systematic study of the properties of the gels derived from various complexing agents has been undertaken in our laboratory. In this paper the characteristics of the gels prepared through acetate, acetate-citrate, nitrate-citrate and acrylamide routes and their effect on the formation of the superconducting 123 phase are discussed.

2. Experimental details

2.1. Materials

Yttrium acetate (Leico Industries, New York, 99.9% pure), barium and copper acetates (Fluka, Switzerland,

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99.9% pure) and yttrium, barium and copper nitrates (BDH, India, 99.5% pure) were used as such without further purification. All other chemicals were of BDH AR or equivalent grade.

2.2. Synthesis

2.2.1. Acetate route

Yttrium, barium and copper acetates, taken in the cation mole ratio of 1:2:3 (5 mmol, 10 mmol and 15 mmol respectively), were dissolved in 80 ml of distilled water and the pH of the mixture solution was adjusted to 7.0 with concentrated ammonia solution. The samples were stirred at 343 K for 3 h and kept in an oven at 343 K for 48 h for gelation.

2.2.2. Acetate–citrate route

Acetates of yttrium, barium and copper in the cation ratio of 1:2:3 (5 mmol, 10 mmol and 15 mmol respectively) were dissolved in 80 ml of distilled water. Citric acid was added to this solution in such a way that at least 1 mol of citric acid was present for every mole equivalent of metal ion present in the solution (72 mmol of citric acid dissolved in a minimum amount of water). The resultant solution was adjusted to pH 7.0 with concentrated ammonia. The solution thus obtained was concentrated at 343 K to produce a viscous slurry and vacuum dried to yield a fine bluish powder.

2.2.3. Nitrate–citrate route

Nitrates of yttrium, barium and copper in the cation mole ratio of 1:2:3 (5 mmol, 10 mmol and 15 mmol respectively) were dissolved in distilled water. Citric acid solution (72 mmol) was added and the pH was adjusted to 7.0 with concentrated ammonia solution. The solution was gelled at 343 K in an oven and decomposition of the gels on a hot plate yielded powdered samples.

2.2.4. Acrylamide route

Acetates of yttrium acetate, barium acetate and copper acetates were dissolved in 80 ml of distilled water in the cation mole ratio of 1:2:3 (5 mmol, 10 mmol and 15 mmol respectively) and 72 mmol of citric acid solution were added to this mixture solution. The pH of the solution was then adjusted to 7.0 by adding concentrated ammonia. To this solution acrylamide (12.0 g), methylene-bisacrylamide (1.0 g), tetramethylethylenediamine (0.4 ml) and hydrogen peroxide (4.0 ml of 3% solution) were added and the solution was held at 343 K for gelation. The gel thus obtained was decomposed on a hot plate to yield fine powders.

All the samples were decomposed at 723 K for 12 h followed by calcination at 1173 K for 24 h in air. The powders thus obtained were compacted at 300 MPa and subsequently sintered at 1173 K for 24 h and

at 1223 K for 24 h in oxygen environment. The samples were slowly cooled to room temperature.

2.3. Characterization techniques

The gel samples obtained at 343 K have been characterized. IR spectra ($4000\text{--}400\text{ cm}^{-1}$) of the gel samples were taken in KBr pellets at room temperature using a Hitachi 270-30 spectrometer. Electronic spectra ($900\text{--}200\text{ nm}$) were recorded as nujol mulls on a Hitachi 330 spectrophotometer. Electron spin resonance (ESR) spectra were recorded at room and liquid nitrogen temperatures on a Varian E-112 spectrometer. Scanning electron micrographs of the gels were obtained using a Philips PSEM 502 instrument. The samples for scanning electron microscopy (SEM) were prepared by spraying the gel powders onto a glass plate. The specimens were gold coated before subjecting them to SEM. X-ray diffraction (XRD) patterns of the gels, as well as the heat-treated samples, were obtained using a Siemens 500D diffractometer with $\text{Cu K}\alpha$ radiation. Resistivity measurements on the sintered samples were conducted using the van der Pauw four-probe method. A.c. susceptibility measurements were carried out on oxygenated powders. The volume fractions of the superconducting phases were evaluated taking niobium powder as standard.

3. Results and discussion

3.1. IR spectra

The IR spectra of the gels derived from acetate, acetate–citrate, nitrate–citrate and acrylamide routes are shown in Fig. 1. Three well-defined bands at 3318, 3229, 3169 cm^{-1} are assignable to the weakly hydrogen-bonded water molecules in the acetate gel. These characteristic bands are similar to those found in the cupric acetate monohydrate [11] indicating that the identity of the salt is reappearing in the gel. The broad bands observed in the spectra of all the remaining gels at around 3150 cm^{-1} have been assigned to O–H stretching frequencies $\nu(\text{O–H})$ of the intermolecular hydrogen-bonded water.

The band at 471 cm^{-1} in the acetate gel (Fig. 1(b)) has been assigned to the M–O stretching frequency of yttrium acetate, suggesting the presence of free yttrium acetate in the gel. However, it has not been possible to assign the bands appearing below 600 cm^{-1} in the spectra of all the remaining gels to any individual $\nu(\text{M–O})$ vibrations. This is because of the presence of three COO^- groups in citrate and one COO^- group in acetate with their possible unidentate, bidentate, chelating and/or bridging coordination with any one or more of the available metal ions present in the gels.

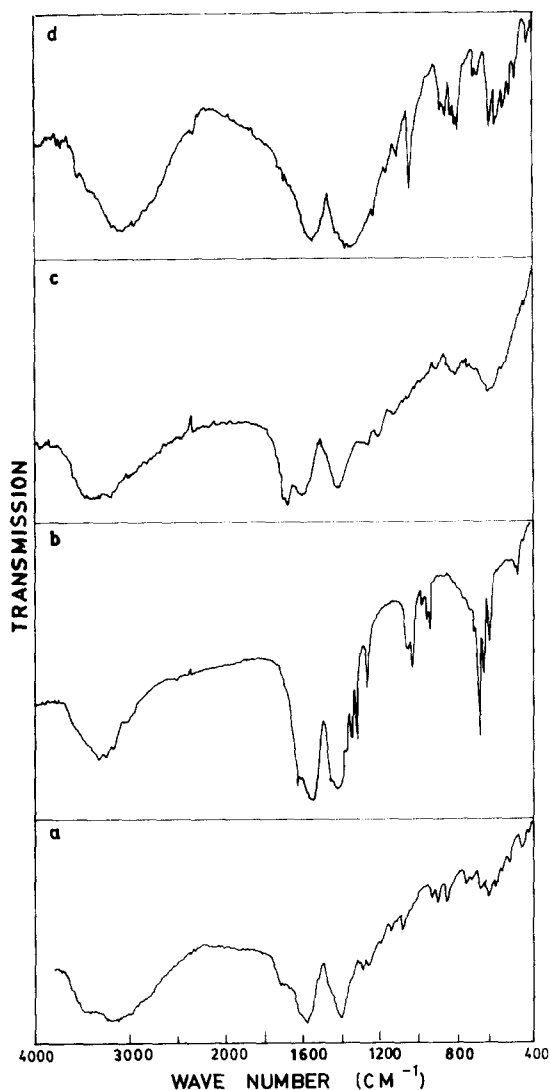


Fig. 1. IR spectra of various gel samples: (a) acetate-citrate; (b) acetate; (c) acrylamide; (d) nitrate-citrate.

Therefore, these peaks have been tentatively assigned to $\nu(\text{M-O})$ [12]. The peaks responsible for carboxylate and nitrate ions could be identified in the spectra and therefore they are discussed in detail.

The IR spectra of all the gels show two bands in the $1559\text{--}1590\text{ cm}^{-1}$ and $1410\text{--}1420\text{ cm}^{-1}$ regions assignable to asymmetric and symmetric vibrations of the COO^- ion (ν_a and ν_s) respectively. According to Deacon and Phillips, the separation $\Delta\nu$ between ν_a and ν_s is an indication of the type of carboxylate group bonding in metal carboxylates [13]. From a number of metal carboxylates of well-established crystal structures, it was concluded that a $\Delta\nu$ value of more than 200 cm^{-1} indicates unidentate coordination, less than 105 cm^{-1} suggests chelation and a value between 105 and 200 cm^{-1} is indicative of the presence of bridging and/or chelating coordination of the carboxylate group. A $\Delta\nu$ value of $139\text{--}170\text{ cm}^{-1}$ obtained in the spectra of all the gels indicates that the bonding of the carboxylate

group in these gels is either bridging or chelating in nature. In addition to the above, the IR spectrum of the acetate-citrate gel (Fig. 1(a)) shows two well-defined peaks at 1720 cm^{-1} and 1300 cm^{-1} assignable to ν_a and ν_s ($\Delta\nu=420\text{ cm}^{-1}$) respectively, suggesting unidentate coordination [14], in addition to the bridging or chelating COO^- groups in this gel. The well-defined band observed at 1680 cm^{-1} in the IR spectrum of acrylamide gel (Fig. 1(c)) could not be assigned to ν_a of the unidentate COO^- group because the corresponding ν_s in the $1300\text{--}1340\text{ cm}^{-1}$ region is absent. Therefore, this band has been assigned to $\nu(\text{C=O})$ of the amide group. However, since the peaks due to N-H stretching vibrations have been obscured by the presence of a broad band owing to $\nu(\text{O-H})$, the bonding behaviour of the amide NH_2 group could not be established in acrylamide gel.

Three bands at 1384 , 832 and 728 cm^{-1} , observed only in the spectra of nitrate-citrate gel (Fig. 1(d)), have been assigned to ν_2 , ν_1 and ν_3 vibrations of free nitrate ion following the assignments given by Addison and Logan [15]. Since both the carboxyl OH and hydroxyl OH of citric acid are completely deprotonated at pH 7.0 [16], the citrate ion becomes strongly coordinating towards metal ions when compared with the nitrate ion at the same pH. It has been therefore inferred that only citrate ion is involved in coordination with the available metal ions in the gel and that the nitrate ion has reacted with ammonia (used for adjusting pH) to form ammonium nitrate. The formation of ammonium nitrate is also supported by the fact that gels prepared through the nitrate-citrate route caught fire while being heated on a hot plate.

3.2. Electronic spectra

The electronic spectra of the gel samples are shown in Fig. 2. The band positions obtained from the electronic spectra of all the gel samples together with those reported for copper(II) acetate and copper(II) citrate are shown in Table 1. It was reported that the electronic spectrum of dimeric copper(II) acetate shows a broad band at $14\,300\text{ cm}^{-1}$ assigned to the $d_{z^2} \rightarrow d_{x^2-y^2}$ transition together with the carboxylate-copper(II) charge transfer band at $40\,820\text{ cm}^{-1}$. In addition to these two bands, the characteristic absorption band due to the antiferromagnetic coupling of the copper(II) ions within the dimer was reported at $27\,400\text{ cm}^{-1}$ [17]. Similarly, the electronic spectrum of the dimeric copper(II) citrate complex also shows the d-d transition band at $12\,900\text{ cm}^{-1}$ together with its charge transfer band at $40\,000\text{ cm}^{-1}$. However, the expected dimeric peak at around $27\,000\text{ cm}^{-1}$ was absent in the spectrum owing to the non-coplanarity of the copper ions in the dimer [18].

The electronic spectrum of the acetate gel (Fig. 2, spectrum c) shows a broad asymmetric band centred

Table 1
Absorption and electron spin resonance data of various gel samples

Sample number	Sample	d-d transition $d_{x^2-y^2}-d_{z^2-y^2}$ (cm^{-1})	Charge transfer band (cm^{-1})	Dimeric peak (cm^{-1})	g_{\parallel}	g_{\perp}
1	Copper citrate ^a	12 900	40 000	–	1.98	2.45
2	Copper acetate ^b	14 300	40 820	27 400	2.42	2.08
3	Acetate gel	15 000	40 000	–	2.21, 2.13, 2.05	
4	Nitrate-citrate gel	13 986	36 363	–	2.23	2.05
5	Acetate-citrate gel	13 888	41 666	26 300	2.42	2.05
6	Acrylamide gel	15 151	37 037	–	2.38	2.05

^a Ref. 18.

^b Ref. 17.

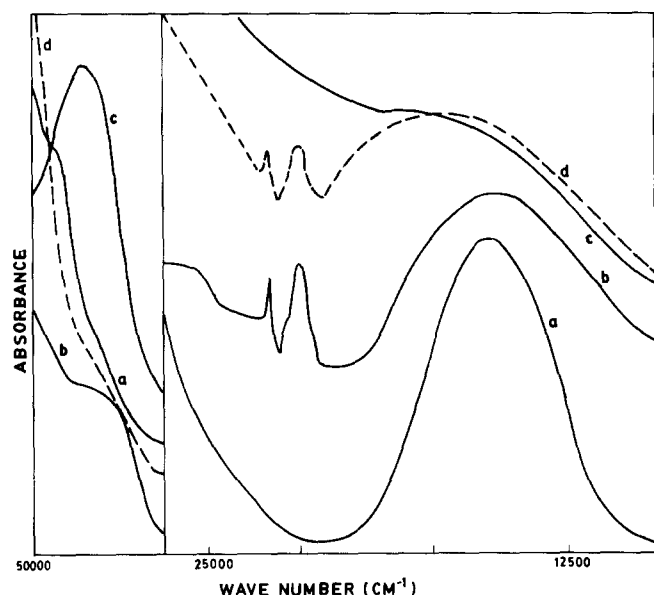


Fig. 2. The electronic spectra of the gels derived from different routes showing the d-d transition band of copper ions: spectrum a, nitrate-citrate; spectrum b, acetate-citrate; spectrum c, acetate; spectrum d, acrylamide.

at $15\,000\text{ cm}^{-1}$ assignable to the d-d transition and an absorption at $40\,000\text{ cm}^{-1}$ due to the L→M charge transfer transition. There has been no appreciable change in the positions of these two bands when compared with those found in the copper(II) acetate spectrum indicating that copper(II) acetate molecules are segregated in the acetate gel. The electronic spectrum of the nitrate-citrate gel (Fig. 2, spectrum a) has yielded a well-defined d-d transition band of copper(II) at $13\,980\text{ cm}^{-1}$ and the corresponding charge transfer band at $36\,360\text{ cm}^{-1}$. A blue shift in the d-d transition band shows that the tetragonal distortion around the copper(II) ion is increased in the gel when compared with that present in the copper citrate [19]. A red shift in the charge transfer band is due to a weaker coordination of the citrate ion in the gel compared with that present in copper(II) citrate complex. Since the

IR spectral studies have shown that the nitrate ions are not involved in complexation, the increased distortion in the stereochemistry of copper(II) ions and the weaker coordination of the citrate ions could be due to the bridging of the citrate ions with other metal ions also present in the gel (see ESR spectra in Section 3.3).

The two bands at $13\,888\text{ cm}^{-1}$ and $41\,666\text{ cm}^{-1}$ obtained in the electronic spectrum of acetate-citrate gel (Fig. 2, spectrum b) have been assigned to the d-d and L→M charge transfer transitions respectively. In addition to the above, a peak at $26\,300\text{ cm}^{-1}$ which could be due to the presence of copper(II)-copper(II) dimers has also been observed in the electronic spectrum of this gel, indicating that the identity of the dimeric copper(II) acetate is retained in the gel. The positions of the d-d and charge transfer bands indicate that the extent of distortion around the copper(II) ion and the complexation of the anions in this gel are between those found in the copper(II) acetate and copper(II) citrate complexes.

The broad and well-defined band at $15\,151\text{ cm}^{-1}$ in the electronic spectrum of acrylamide gel (Fig. 2, spectrum d) has been assigned to the d-d transition within the copper(II) ions and that obtained at $37\,037\text{ cm}^{-1}$ has been assigned to the L→M charge transfer band. Since the amide coordination in this gel could be neither established nor ruled out, a comparison of the extent of bonding with respect to the copper(II) acrylamide could not be made. However, the absence of a dimeric peak in the electronic spectrum of this gel shows that the identity of copper dimers present in the copper(II) acetate is lost because of the formation of a homogeneous gel due to the presence of an acrylamide polymeric network.

The electronic spectra of the acetate-citrate and the acrylamide gels have also yielded two sharp bands at $20\,000$ and $21\,500\text{ cm}^{-1}$ which are uncharacteristic of d-d transitions. The origin of these bands is not known.

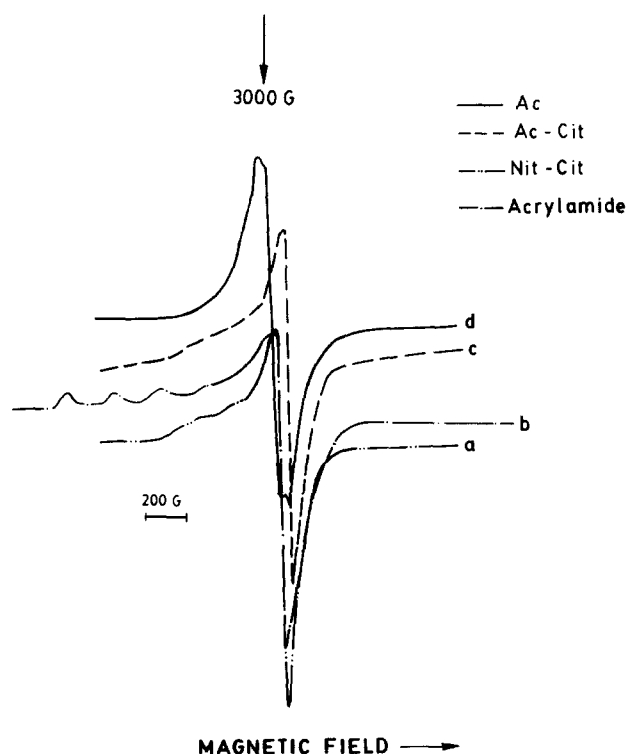


Fig. 3. ESR spectra of different gel samples: spectrum a, nitrate–citrate; spectrum b, acrylamide; spectrum c, acetate–citrate; spectrum d, acetate.

3.3. Electron spin resonance spectra

The ESR spectra of the gel samples are shown in Fig. 3 and the g values evaluated from the spectra are included in Table 1. Table 1 shows that the three g values of the acetate gel are characteristic of a rhombic distortion around copper(II), while those of the nitrate–citrate, acetate–citrate and acrylamide gels are consistent with an elongated octahedral stereochemistry around copper(II) with $g_{\parallel} > g_{\perp} > 2.00$.

It was reported that the presence of non-transition metal ions in copper(II) citrate solutions brings about an unexpected complexity in the structure of the chelates [20,21]. For example, the g values for Cu(II) citrate in aqueous and non-aqueous solutions lie in the $g_{\parallel} = 1.98\text{--}2.09$ and $g_{\perp} = 2.20\text{--}2.45$ ranges (compressed octahedral stereochemistry), while those for Cu(II) citrate in the presence of Al(III) or Hg(II) ions are $g_{\parallel} = 2.34$ and $g_{\perp} = 2.07$ (elongated octahedral geometry) [20]. Such a reversal of axial symmetry around Cu(II) ion is interpreted in terms of the formation of a structural framework involving the uncoupled copper(II) citrate molecules bridged by the heterometal ions [21].

The g values of copper(II) obtained for the nitrate–citrate gel (Table 1) suggest that the individual ion site symmetry has changed from the compressed octahedral stereochemistry observed in the copper(II)

citrate complexes to that with an elongated octahedral geometry in the gel. It can therefore be inferred that the gel contains Ba^{2+} (or Y^{3+}) and Cu^{2+} ions which are bridged by citrate ions giving a homogeneous distribution of metal ions in the gel. A similar network of metal ions might have been possible in the acrylamide gel creating an organic polymer which is a priori chemically independent of other species present in the solution. The parallel and perpendicular features of copper(II) are therefore clearly resolved in the ESR spectrum of acrylamide gel (Fig. 3, spectrum b) because of such a polymeric network.

The g values for acetate–citrate gel (Table 1) have been found to be similar to those reported for copper(II) acetate [17], indicating the persistence of copper acetate dimers in the gels. This is also in accordance with the observation of a dimeric peak in the electronic spectrum (Fig. 2, spectrum b). Thus, both the ESR and the electronic spectra suggest that copper(II) acetate aggregates which eventually lead to more impurity phases in the final product when compared with those obtained from nitrate–citrate and acrylamide routes are present in the acetate–citrate gel.

3.4. X-ray diffraction

The phases identified by XRD patterns of the samples after heat treatment at various temperatures and the lattice parameters evaluated from the diffractograms of the oxygenated samples of 123 phase are shown in Table 2. The XRD patterns of the samples heat treated at 1173 K for 24 h in air are shown in Fig. 4. It can be seen from Table 2 that all the gel powders are amorphous at room temperature (300 K) and the three Y_2O_3 , BaCO_3 and CuO phases are formed on heat treatment at 723 K. The Y_2BaCuO_5 (211) impurity phase has been formed at 1173 K in the sample derived from acetate gel, whereas BaCuO_2 has been precipitated as an impurity phase in the samples prepared from both nitrate–citrate and acetate–citrate gels (Fig. 4). However, at this temperature, the sample prepared through the acrylamide gel route yielded pure 123 compound.

When the samples are further heated to 1223 K in an oxygen atmosphere, the BaCuO_2 phase has disappeared in the samples prepared through nitrate–citrate and acetate–citrate gel routes. However, the 211 phase obtained in the acetate-derived sample has been persistent even after heat treatment in an oxygen atmosphere. This persistence is due to the fact that, once the 211 phase is trapped inside the grains of 123 phase, it is very difficult for it to convert to the 123 compound [22]. A detailed investigation carried out by the present authors on the effect of pH on the formation of the 123 compound through acetate gel routes has shown

Table 2
Phases formed in various gel samples at different temperatures

Sample number	Gel route	Phases formed at the following temperatures (K)				Lattice parameters (Å)
		300	773	1173	1223	
1	Acetate (pH 7.0)	Amorphous	Y ₂ O ₃ , BaCO ₃ , CuO	123, 211	123, 211	3.845, 3.871, 11.657
2	Nitrate-citrate	Amorphous	Y ₂ O ₃ , BaCO ₃ , CuO	123, BaCuO ₂	123	3.813, 3.875, 11.65
3	Acetate-citrate	Amorphous	Y ₂ O ₃ , BaCO ₃ , CuO	123, BaCuO ₂	123	3.825, 3.875, 11.65
4	Acrylamide	Amorphous	Y ₂ O ₃ , BaCO ₃ , CuO	123		3.808, 3.88, 11.678

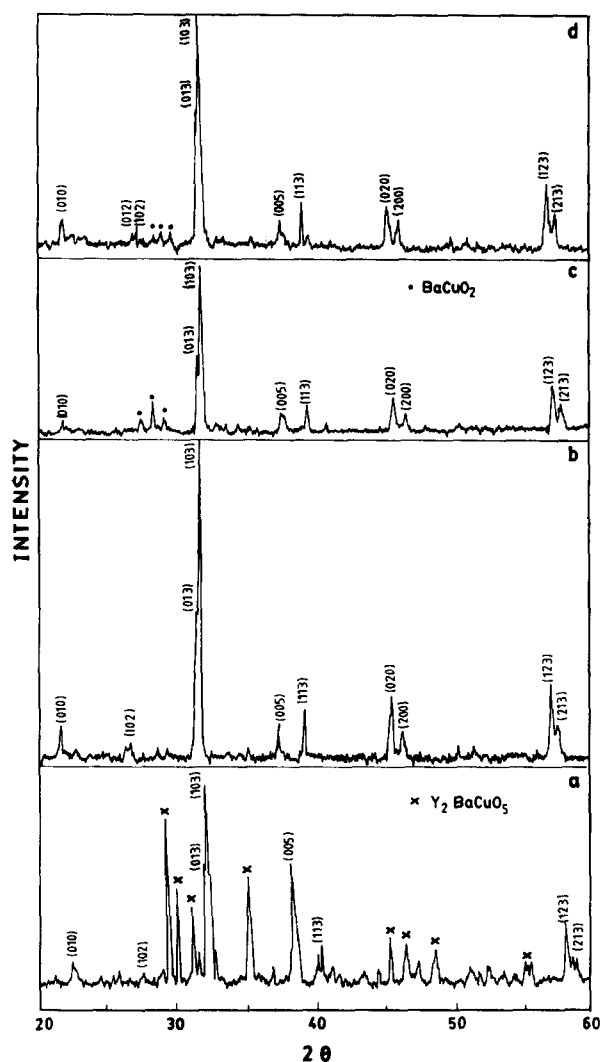


Fig. 4. XRD patterns of gel samples heat treated at 1173 K for 24 h in air showing the formation of 123 compound: (a) acetate; (b) acrylamide; (c) acetate-citrate; (d) nitrate-citrate routes.

that it is possible to avoid the formation of 211 phase by maintaining the initial pH of the mixture at 6.0 [8].

3.5. Scanning electron microscopy

Typical scanning electron micrographs of the gel powders (after drying at 343 K) are shown in Fig. 5. The electron micrographs of sintered pellets derived

from the four gel routes are shown in Fig. 6. Fig. 5 indicates that particles are agglomerated in all the gel samples and the particle size lies in the range 0.1–0.5 μm . A fibrous structure is observed for the gels derived from acetate-citrate and acrylamide gel routes. It was reported that dense and large grain size structures in the materials are favourable for obtaining stable, high performance superconducting properties [23]. It is obvious from the micrographs that larger grains and dense structures are observed in the samples prepared from acetate-citrate, nitrate-citrate and acrylamide gels compared with the samples prepared from acetate gels.

3.6. Resistivity and susceptibility

The normalized resistivity vs. temperature characteristics of superconducting samples obtained from different gel routes are shown in Fig. 7. Samples derived from the acetate route (Fig. 7) show the lowest superconducting transition temperature $T_{c, \text{zero}} = 79$ K whereas the other samples show the transition temperature at 90 K. XRD studies indicate that samples obtained from the acetate route with pH 7.0 contained large amounts of 211 phase which might be the reason for the lower superconducting transition temperature. Samples prepared from the acetate-citrate, acrylamide and nitrate-citrate gel routes showed sharp superconducting transitions with $\Delta T_c = 3$ K indicating the homogeneity of the phases. The normalized a.c. susceptibility vs. temperature $\chi-T$ plots are given in Fig. 8. The diamagnetic onset agrees well with $T_{c, \text{zero}}$ from $\rho-T$ studies except in the case of the acetate gel-derived (Fig. 8) sample which shows a broad transition in the $\chi-T$ plots. The sample derived from the acrylamide gel route shows the sharpest transition and this observation correlates well with our observations from the XRD and spectral studies. The per cent volume fractions of superconducting phases evaluated from susceptibility measurements are 52, 64, 65 and 75, corresponding to samples derived from acetate, acetate-citrate, nitrate-citrate and acrylamide gel routes respectively.

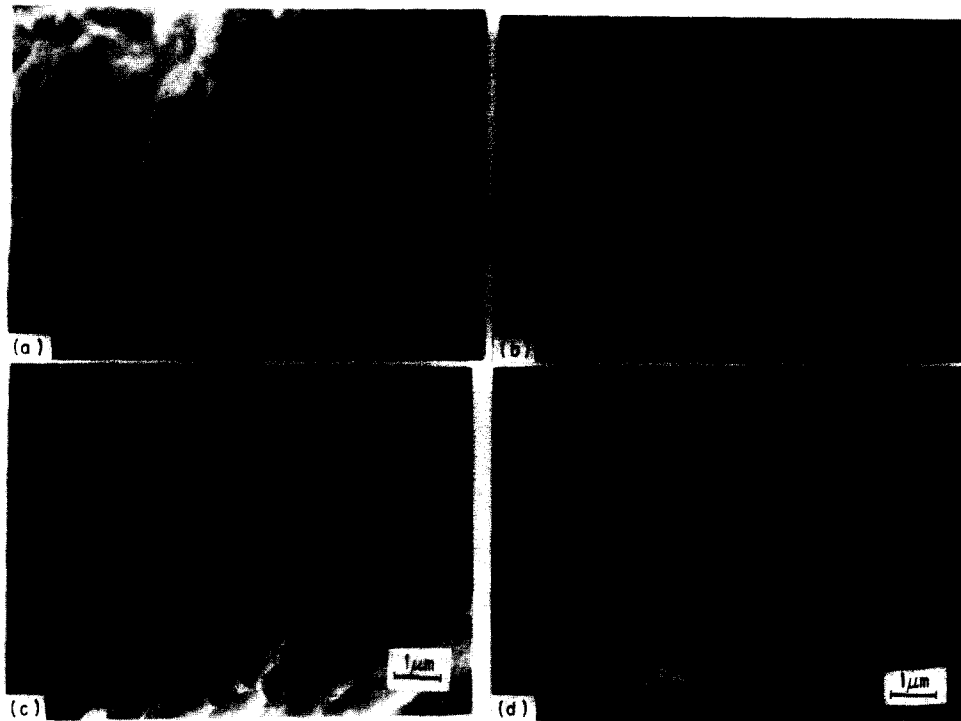


Fig. 5. SEM images of gels derived from various routes: (a) acetate; (b) acrylamide; (c) nitrate-citrate; (d) acetate-citrate.

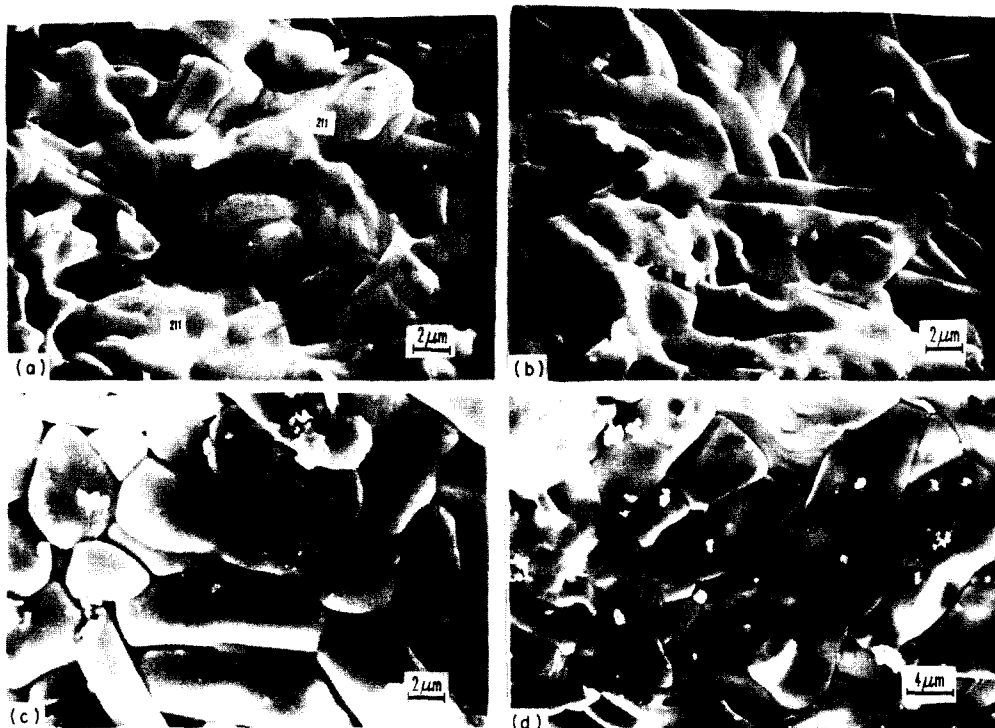


Fig. 6. Scanning electron micrographs of 123 sintered pellets synthesized from different gel routes showing large elongated grains: (a) acetate; (b) acrylamide; (c) nitrate-citrate; (d) acetate-citrate.

4. Conclusions

In the synthesis of 123 compound by the sol-gel route, the phase purity of the final product depends

very much on the homogeneity of the gel. A homogeneous distribution of the metal ions in the gel as in the case of the acrylamide gel (characterized by the absence of free metal acetates or citrates) leads to the

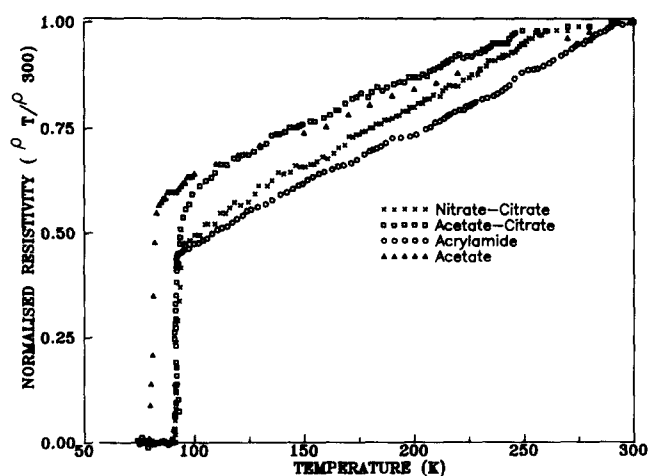


Fig. 7. Normalized resistivity–temperature plots of 123 samples derived from different gel routes showing the superconducting transition.

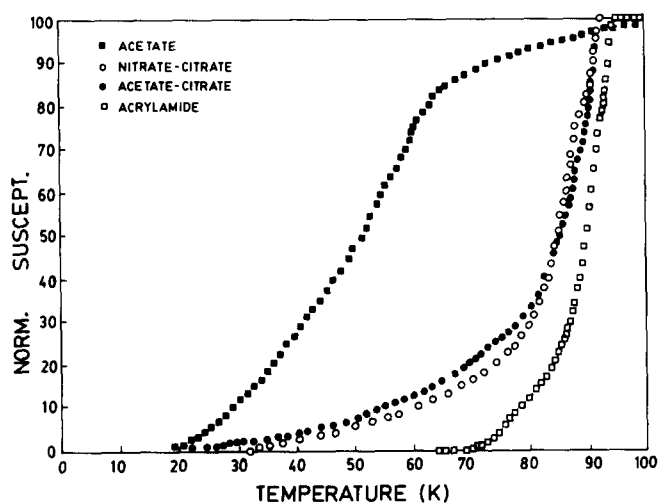


Fig. 8. Normalized susceptibility–temperature plots showing the diamagnetic transition of 123 compound prepared from various gel routes.

formation of the phase-pure 123 compound exhibiting a maximum T_c of 90 K with $\Delta T_c = 1.2$ K. In the nitrate–citrate gel also, the presence of a heterometallic framework involving barium (or yttrium) and copper ions leads to a homogeneous distribution of metal ions which prevents the formation of 211 impurity phase in the final product.

On the contrary, the presence of individual metal acetates in the acetate gel brings about an inhomogeneous distribution of metal ions in the gel leading to the formation of the 211 impurity phase in the final product. This impurity phase is persistent even after the heat treatment of the samples at 1223 K for 24 h in an oxygen atmosphere.

The acetate–citrate gel shows the presence of copper dimers in the gel, as is found in the acetate gel indicating inhomogeneity. Thus, even though the formation of the 211 impurity phase is predicted owing to the presence

of dimers in this gel, the citrate ion coordination in the gel might have prevented the formation of this phase. Nevertheless, the quantity for the BaCuO_2 impurity phase is larger in the final product obtained from the acetate–citrate gel when compared with that obtained from the nitrate–citrate gel which disappears on heat treatment at 1223 K for 24 h in both of the cases.

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References

- [1] M.K. Wu, J.R. Ashburn, C.J. Torng, P.H. Hor, R.L. Meng, L. Gao, Z.L. Huang, Y.Q. Wang and C.W. Chu, *Phys. Rev. Lett.*, **58** (1987) 908.
- [2] U.V. Varadaraju and G.V. Subba Rao, in A. Narlikar (ed.), *Studies of High Temperature Superconductors*, Nova Science, New York, 1989, p. 229.
- [3] R. Pankajavalli, J. Janaki, O.M. Sreedharan, J.B. Gnanamoorthy, G.V.N. Rao, V. Sankara Sastry, M.P. Janwadkar, Y. Hariharan and T.S. Radhakrishnan, *Physica C*, **156** (1988) 737.
- [4] P.L. Villa, S. Zannella, V. Ottoboni, A. Ricca, N. Ripamonti and M. Scaglioti, *J. Less-Common Met.*, **150** (1989) 299.
- [5] P. Ravindranathan, S. Komaraneni, A. Bhalla, R. Roy and L.E. Cross, *J. Mater. Res.*, **3** (1988) 810.
- [6] E.A. Hayri, M. Greenbalt, K.V. Ramanujachary and R. Gerhart, *J. Mater. Res.*, **4** (1989) 1009.
- [7] H. Kozuka, T. Omeda, J. Jin, T. Monde and S. Sakka, *Bull. Inst. Chem. Res., Kyoto Univ.*, **66** (1988) 80.
- [8] G.V. Rama Rao, D.S. Surya Narayana, U.V. Vardaraju and S. Venkadesan, *Mater. Chem. Phys.*, in press.
- [9] A. Douy and P. Odier, *Mater. Res. Bull.*, **24** (1989) 1119.
- [10] L.L. Hench and J.K. West, *Chem. Rev.*, **90** (1990) 33.
- [11] A.H. Heyn, *J. Mol. Struct.*, **11** (1972) 93.
- [12] K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, Wiley, New York, 3rd edn., 1978.
- [13] G.B. Deacon and R.J. Phillips, *Coord. Chem. Rev.*, **33** (1980) 227.
- [14] S. Dœuff, M. Henry, C. Sanchez and J. Livage, *J. Non-Cryst. Solids*, **89** (1987) 206.

- [15] C.C. Addison and N. Logan, *Adv. Inorg. Chem. Rad. Chem.*, 6 (1964) 72.
- [16] R.W. Parrr and F.W. Dubois, *J. Am. Chem. Soc.*, 74 (1952) 3749.
- [17] M.L. Tonnet, S. Yamada and I.G. Ross, *Trans. Faraday Soc.*, 60 (1964) 840.
- [18] D. Masteropaolo, D.A. Powers, J.A. Potenza and H.J. Schugar, *Inorg. Chem.*, 15 (1976) 1444.
- [19] A.B.P. Lever, *Inorganic, Electronic Spectra*, Elsevier, Amsterdam, 2nd edn., 1984, p. 554.
- [20] R.C. Srivastava, T.D. Smith, J.F. Boas, T. Lund, J.H. Price and J.R. Pilbrow, *J. Chem. Soc. A*, (1971) 2538.
- [21] T.D. Smith and J.R. Pilbrow, *Coord. Chem. Rev.*, 13 (1974) 232.
- [22] G. Selvaduray, C. Zhang, U. Balachandran, Y. Gao, K.L. Merkle, H. Shi and R.B. Poeppel, *J. Mater. Res.*, 7 (1992) 283.
- [23] M. Kuwabara, *Jpn. J. Appl. Phys.*, 26 (1987) L1821.