

# Solution spinning of a high- $T_c$ oxide superconductor: 5. The influence of yttrium and barium ions on the poly(vinyl alcohol)–copper(II) complex

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The interaction of Y(III) and Ba(II) ions in the solid poly(vinyl alcohol) (PVA)–copper(II) acetate system with propionic acid was studied. Two kinds of coordination structures were detected in the films cast from an aqueous solution containing PVA and copper(II) acetate. One was a mononuclear Cu(II) complex, with the other being a binuclear Cu(II) complex of the cupric-acetate type. A significant decrease in the amounts of both of these complexes was observed on the addition of Y(III) and Ba(II) ions because of the formation of a multimetal polynuclear complex. The solubility of copper(II) acetate in aqueous PVA solution was increased by adding yttrium and barium acetates and attained its maximum level at a molar ratio of [Y]:[Ba]:[Cu] = 1:2:3. A precursor  $Y_1Ba_2Cu_3O_x$  filament containing a large quantity of Y(III), Ba(II) and Cu(II) ions was shown to be beneficial for the generation of the superconducting phase by heat treatment.

(Keywords: PVA–Cu(II) complex; oxide precursor; superconductor)

## INTRODUCTION

We have studied the preparation of high- $T_c$  oxide superconducting long filaments by using textile fibre spinning technology for the precursor of the oxide. In our previous study, the Y–Ba–Cu–O filament was prepared by dry-spinning, starting from a homogenous aqueous solution containing the acetates of Y, Ba and Cu, poly(vinyl alcohol) (PVA) and propionic acid<sup>1</sup>. The superconducting properties of the heated filament depend on the spinning dope composition as well as on the spinning conditions and the heat treatment. As basic research into the solution spinning technique, the interaction between PVA and copper(II) acetate in aqueous solution and in the solid state, both with and without propionic acid, has been studied. It was found that interactions between PVA and Cu(II) ions in aqueous solution were non-existent under the experimental conditions employed, while the formation of a complex of PVA with Cu(II) ions was observed by casting the film from solution. The addition of propionic acid increased the solubility of the copper(II) acetate in the aqueous solution<sup>2</sup>. In this present paper, the Cu(II)–PVA complex structure is examined by using electron spin resonance (e.s.r.) spectroscopy. The influence of Y(III) and Ba(II) ions on the Cu(II)–PVA complex is

also studied in order to clarify the microstructure of the precursor  $Y_1Ba_2Cu_3O_x$  filament.

## EXPERIMENTAL

PVA (degree of polymerization,  $\bar{P} = 1700$ ) was supplied by Nitivy Co. Ltd, and had a degree of saponification of 85 mol%, as determined by <sup>1</sup>H nuclear magnetic resonance (n.m.r.) spectroscopy. PVA samples where  $\bar{P} = 500$  and 4000, with a degree of saponification of 100 mol%, were obtained commercially (Wako Co. Ltd) and copper(II) acetate monohydrate (99.9%), anhydrous barium acetate (99.9%), yttrium acetate *n*-hydrate (99.99%) and propionic acid (analytical grade) were used without further purification.

The sample films were cast at 80°C on a polyethylene substrate, after deaerating aqueous solutions containing 2.0 mol l<sup>-1</sup> PVA, 0.2–0.6 mol l<sup>-1</sup> copper(II) acetate, 0–0.6 mol l<sup>-1</sup> barium acetate and 0–0.6 mol l<sup>-1</sup> yttrium acetate with propionic acid. The solutions were adjusted to pH 4.3 by adding propionic acid.

E.s.r. and ultra-violet/visible (u.v./vis) spectra were measured in order to reveal the behaviour of the Cu(II) ions. E.s.r. spectra for the films were obtained with a JEOL X-band spectrometer (model JES-FE-1XG) equipped with a 100 kHz field modulation. The magnetic field was calibrated with 0.1 mol% Mn(II) (MgO) and an X-band frequency counter. U.v./vis spectra of the films

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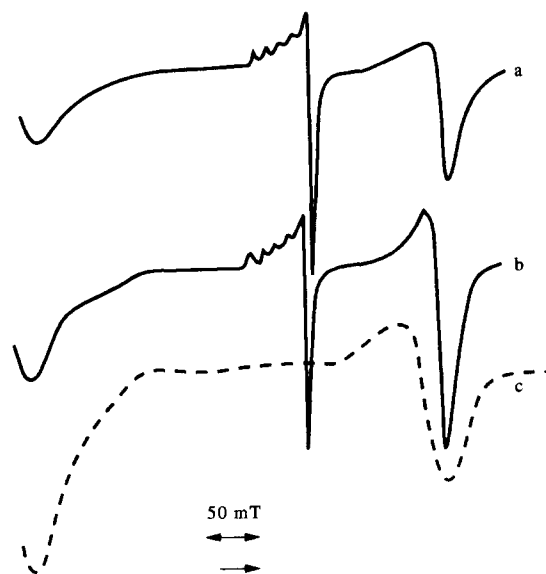
were recorded on a Shimadzu UV-1200 instrument in the region from 300 to 900 nm.

A Shimadzu 408 instrument was used for infra-red (i.r.) spectroscopy. The films were dissolved in  $D_2O$  and  $^1H$  n.m.r. spectra of  $D_2O$  solutions of the films were recorded on a Varian XL-200 (200 MHz) spectrometer. X-ray diffraction (Rigaku Denki Co. Ltd) was used to investigate the structure of the films, employing  $CuK\alpha$  radiation.

## RESULTS AND DISCUSSION

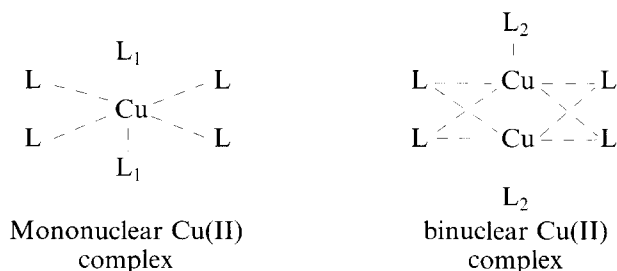
### *Cu(II)-PVA complex*

It was previously reported that the  $Cu(II)$ -PVA complex structure in the film was changed on the addition of propionic acid from one in which the  $Cu(II)$  ion coordinates to the hydroxy groups on PVA to a form where the  $Cu(II)$  ion complexes with two acetate ions in addition to the hydroxy groups<sup>2</sup>. E.s.r. measurements on the PVA- $Cu(II)$  film at a molar ratio of  $Cu(II)$  ion to PVA ( $[Cu]/[OH]$ ) of 0.11, with and without propionic acid, were carried out. E.s.r. spectra of the films at room temperature in a magnetic field of 300 mT with a magnetic field sweep  $\pm 250$  mT are shown in *Figure 1*. A clearly anisotropic peak with four partially resolved hyperfine lines near 320 mT is observed. In addition, one significant signal in the lowest field and another in the high-field side are observed, as well as the peaks near 320 mT. The spectra near 320 mT are due to the mononuclear  $Cu(II)$  complex. This is only the case when the  $Cu(II)$  ion is directly coordinated to the hydroxy groups in the polymeric ligand. The spectra are characteristic of the tetragonal or almost tetragonal  $Cu(II)$  complex parallel to the  $x$ - and  $y$ -orbitals of the  $Cu(II)$  ion<sup>3</sup>. The powder spectrum of copper(II) acetate monohydrate at room temperature is also shown by a broken line in *Figure 1*, for comparison purposes. The peaks, except for that of the mononuclear



**Figure 1** E.s.r. spectra measured at room temperature in a magnetic field of  $\sim 300$  mT with a magnetic field sweep  $\pm 250$  mT of films cast from solutions containing  $2 \text{ mol l}^{-1}$  PVA and  $0.2 \text{ mol l}^{-1}$   $Cu(II)$  acetate, with and without propionic acid: (a) without acid; (b) with propionic acid ( $10 \text{ mol l}^{-1}$ ); (c) copper(II) acetate monohydrate

$Cu(II)$  complex, are similar to the powder spectrum, and are due to a binuclear  $Cu(II)$  complex of the cupric-acetate type<sup>4,8</sup>. The ratio of the binuclear  $Cu(II)$  complex to the mononuclear  $Cu(II)$  complex increases slightly with the addition of propionic acid, as shown in *Figure 1*. E.s.r. spectra of these films at 77 K were also measured, with no significant differences from the spectra in *Figure 1* being observed. Schematic structures of the  $Cu(II)$ -PVA complexes in the films can be considered as follows:



L : polymer ligand or acetate group

$L_1$  : coordinated water

$L_2$  : polymer ligand or coordinated water

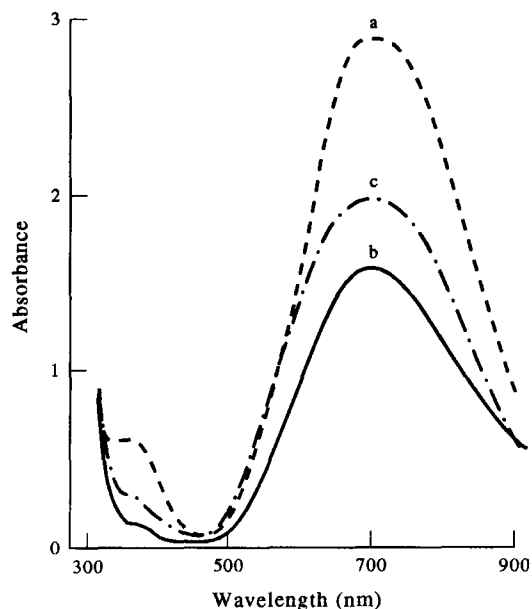
The  $g_{\parallel}$ - and  $g_{\perp}$ -values and  $A_{\parallel}$  values for the mononuclear  $Cu(II)$  complex determined from the spectra are listed in *Table 1*. The  $g_{\perp}$ -value for the tetragonal  $Cu(II)$  complex depends on the donor power of the ligand bound to the metal ion, while the  $g_{\parallel}$ -value is caused by the axial electron state on the plane of this complex. The addition of propionic acid results in a slightly larger  $g_{\perp}$ -value, whereas the  $g_{\parallel}$ -values are identical. This slight change of  $g_{\perp}$ -value is dependent on the different ligands, such as the hydroxy and acetate groups.

The effect of the degree of polymerization ( $\bar{P}$ ) on the  $Cu(II)$ -PVA complex formation was studied, with the following results being obtained; the amount of the complex in the film without propionic acid reached a constant level at  $[Cu]/[OH] > 0.05$ , while the amount of complex increased along with an increase in the  $Cu(II)$  ion content through the addition of propionic acid. On the other hand, the amount of complex increased while the degree of polymerization for the film without

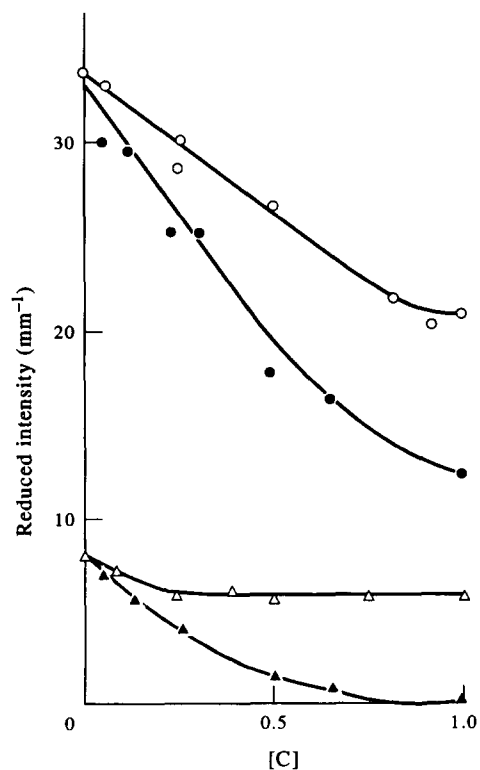
**Table 1** The  $g_{\perp}$  and  $g_{\parallel}$ -values, and values for the  $Cu(II)$  ion hyperfine coupling constant  $A_{\parallel}$  obtained from the e.s.r. spectra of PVA- $Cu(II)$ , films with and without propionic acid

| Sample film                     |               |             |                 |                      |
|---------------------------------|---------------|-------------|-----------------|----------------------|
| Degree of polymerization of PVA | $[Cu]/[OH]^a$ | $g_{\perp}$ | $g_{\parallel}$ | $A_{\parallel}$ (mT) |
| Without acid                    |               |             |                 |                      |
| 1700                            | 0.08          | 2.08        | 2.35            | 14.0                 |
| 1700                            | 0.11          | 2.08        | 2.35            | 14.0                 |
| 500                             | 0.11          | 2.07        | 2.35            | 14.0                 |
| 4000                            | 0.11          | 2.09        | 2.35            | 14.0                 |
| With acid                       |               |             |                 |                      |
| 1700                            | 0.08          | 2.09        | 2.35            | 14.0                 |
| 1700                            | 0.11          | 2.09        | 2.35            | 14.0                 |
| 500                             | 0.11          | 2.08        | 2.35            | 14.0                 |
| 4000                            | 0.11          | 2.08        | 2.35            | 14.0                 |

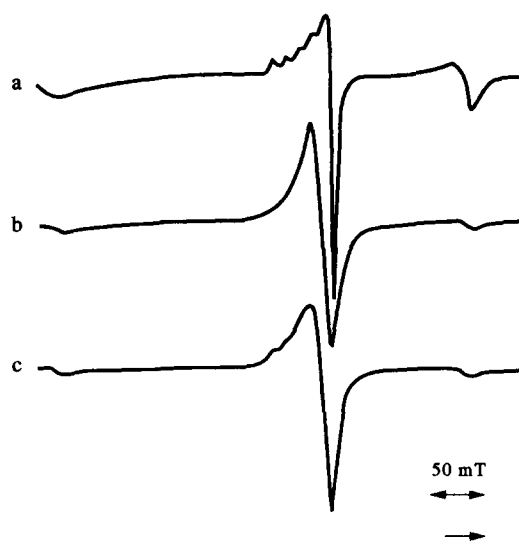
<sup>a</sup> Molar ratio of the  $Cu(II)$  ion to PVA



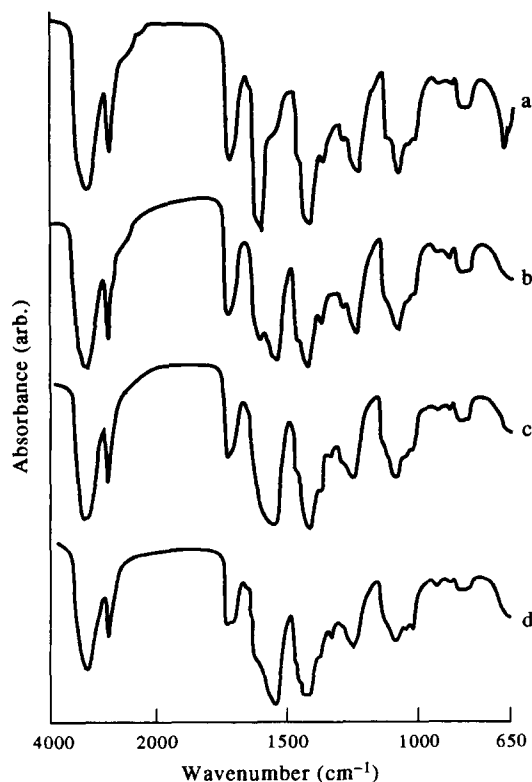
**Figure 2** U.v./vis spectra of films cast from solutions containing  $2 \text{ mol l}^{-1}$  PVA and  $0.2 \text{ mol l}^{-1}$  Cu(II) acetate, plus Y(III) and Ba(II) acetates, adjusted to pH 4.3 by adding propionic acid: (a) [Y]:[Ba]:[Cu] = 1:0:3; (b) [Y]:[Ba]:[Cu] = 0:2:3; (c) [Y]:[Ba]:[Cu] = 1:2:3



**Figure 3** The relationship between the reduced intensity of absorbance at 700 and 370 nm and concentration [C]; the latter is the molar ratio of the Y(III) or Ba(II) ions to Cu(II) ion in films cast from solutions containing  $2 \text{ mol l}^{-1}$  PVA and  $0.2 \text{ mol l}^{-1}$  Cu(II) acetate, plus Y(III) and Ba(II) acetates, adjusted to pH 4.3 by adding propionic acid: (O) at 700 nm for the film containing Y(III) ions; (Δ) at 370 nm for the film containing Y(III) ions; (●) at 700 nm for the film containing Ba(II) ions; (▲) at 370 nm for the film containing Ba(II) ions



**Figure 4** E.s.r. spectra obtained at room temperature over the magnetic field range from 20 to 520 mT of films cast from solutions containing  $2 \text{ mol l}^{-1}$  PVA, Cu(II) acetate,  $0.07 \text{ mol l}^{-1}$  Y(III) acetate and Ba(II) acetate, adjusted to pH 4.3 by adding propionic acid: (a) [Y]:[Ba]:[Cu] = 1:0:3; (b) [Y]:[Ba]:[Cu] = 0:2:3; (c) [Y]:[Ba]:[Cu] = 1:2:3

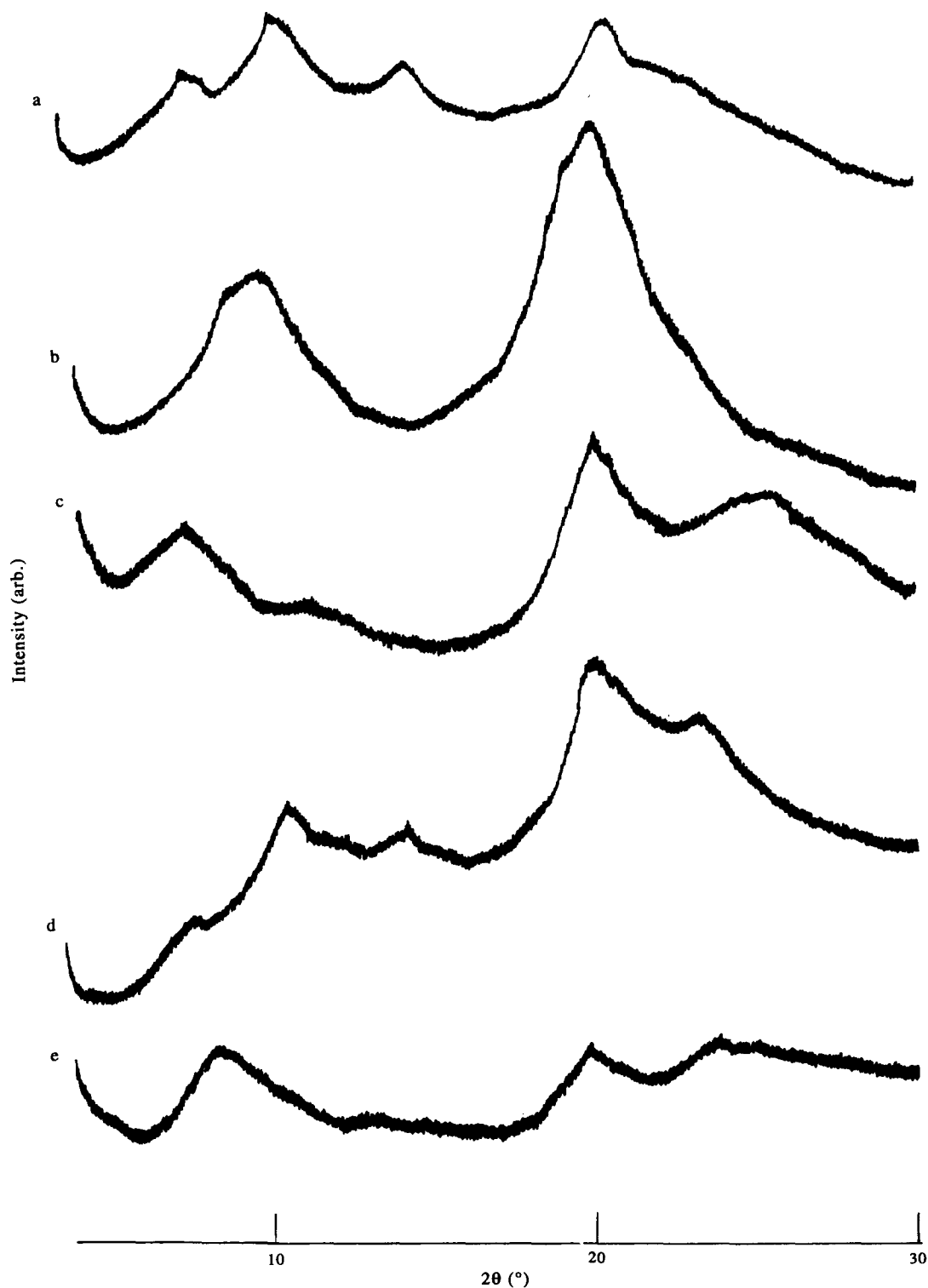


**Figure 5** I.r. spectra of films cast from solutions containing  $2 \text{ mol l}^{-1}$  PVA and  $0.2 \text{ mol l}^{-1}$  Cu(II) acetate, plus Y(III) and Ba(II) acetates, adjusted to pH 4.3 by adding propionic acid: (a) [Y]:[Ba]:[Cu] = 0:0:3; (b) [Y]:[Ba]:[Cu] = 1:0:3; (c) [Y]:[Ba]:[Cu] = 0:2:3; (d) [Y]:[Ba]:[Cu] = 1:2:3

propionic acid decreased. However, the complex reached a maximum value of  $\bar{P} = 1500$  with the addition of propionic acid<sup>9</sup>.

E.s.r. spectra of the PVA-Cu(II) film containing PVA with  $\bar{P} = 500$  and 4000 were also measured and were found to be similar to the spectra shown in Figure 1. The e.s.r. data of the mononuclear Cu(II) complex is also given in Table 1. The  $g_{\parallel}$ -values are independent of the

degree of polymerization. The  $g_{\perp}$ -value of the film without propionic acid increases slightly with an increase in the degree of polymerization, while the  $g_{\perp}$ -value for  $\bar{P} = 4000$  decreases with the addition of propionic acid. Sumita *et al.*<sup>10</sup> proposed structures from e.s.r. measurements for the Cu(II)-PVA complex in the film produced by casting aqueous solutions containing polymer, CuCl<sub>2</sub> (or CuSO<sub>4</sub>) and NaOH at pH > 5. For the case where



**Figure 6** X-ray diffraction patterns (CuK $\alpha$  radiation) for films cast from solutions containing 2 mol l<sup>-1</sup> PVA and/or 0.2 mol l<sup>-1</sup> Cu(II) acetate and/or 0.07 mol l<sup>-1</sup> Y(III) acetate and/or 0.13 mol l<sup>-1</sup> Ba(II) acetate, adjusted to pH 4.3 by adding propionic acid: (a) [Y]:[Ba]:[Cu] = 0:0:3; (b) [Y]:[Ba]:[Cu] = 1:0:0; (c) [Y]:[Ba]:[Cu] = 0:2:0; (d) [Y]:[Ba]:[Cu] = 1:0:3; (e) [Y]:[Ba]:[Cu] = 0:2:3

pH  $\sim$  6, a single Cu(II) ion is coordinated with two water molecules and is chelated with two adjacent oxygen atoms attached to the polymer chain. The complex consisted of a stable hexagonal ring with the polymer chain. As the degree of polymerization of the film without propionic acid in this present work increases, four coordinated ligands one involved in the tetragonal Cu(II) complex, along with each of two adjacent hydroxy groups on the PVA as a result of the chelating effect of the polymer. In the case of the system with propionic acid, formation of the stable hexagonal ring is suppressed at  $\bar{P} = 4000$  because of the entanglement of the polymer chain and the steric hindrance of the bulky acetate groups.

#### *Influence of Y(III) and Ba(II) ions on the Cu(II)-PVA complex in films with propionic acid*

The film cast from an aqueous solution containing PVA, yttrium acetate, barium acetate and copper(II) acetate was green in colour and insoluble in water, but the film produced from the solution with propionic acid was blue in colour and soluble in water. In spite of the addition of Y(III) and Ba(II) ions, the pendant type of complex attached to the linear PVA chain was formed by adding propionic acid.

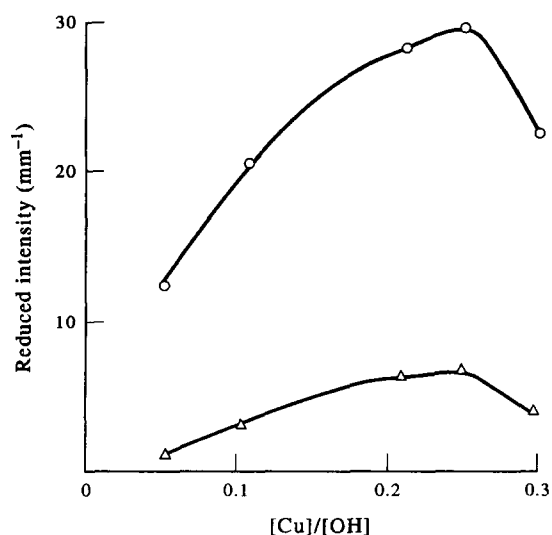
The effect of Y(III) and Ba(II) ions on the complex formation between PVA and Cu(II) ions with propionic acid was examined by u.v./vis spectroscopy. *Figure 2* shows the absorption spectra of the PVA-Cu(II) films containing Y(III) and/or Ba(II) ions. A shoulder-like band at 370 nm, due to the presence of the binuclear Cu(II) complex, is observed along with an isolated copper band at 700 nm. An isolated copper band for the PVA-Cu(II) film was observed at 680 nm<sup>2</sup>. The maximum absorption band in the visible region shifts from 680 to 700 nm with the addition of Y(III) and/or Ba(II) ions. In the case of a PVA-Cu(II) film containing Sr(II) and Ca(II) ions, two absorption bands were observed at 710 and 370 nm<sup>11</sup>. It is well known that this bathochromic shift is caused by the electron-donating group in the metal complex. The shift from 680 to 700–710 nm suggests some interaction between the Cu(II) ions and other ions. *Figure 3* represents the relationship between the reduced intensity of the absorbance at 700 and 370 nm and the content of Y(III) or Ba(II) ions. Here the reduced intensity of the absorbance is given by the absorption intensity per 1 mm thickness of the films, while the content of Y(III) or Ba(II) ions is presented as the molar ratio of these ions to the Cu(II) ion, i.e.  $[Y]/[Cu]$  and  $[Ba]/[Cu]$ . The intensity at 700 nm decreases with an increase in the concentration ratio of the Y(III) ion up to  $[Y]/[Cu] = 0.8$ , while the intensity at 370 nm decreases, reaching a plateau at  $[Y]/[Cu] > 0.2$ . Both of the intensities decrease with an increase in Ba(II) ion content, and the intensity at 370 nm approaches zero at  $[Ba]/[Cu] = 1$ . The addition of these ions tends to prevent the formation of mononuclear and binuclear Cu(II) complexes, with this tendency becoming more significant with the addition of Ba(II) ions.

E.s.r. spectra of the films with Y(III) and/or Ba(II) ions are shown in *Figure 4*. When compared with the spectra shown in *Figure 1*, only one peak near 320 mT is observed and the peaks of the binuclear Cu(II) complex disappear. A distinct anisotropic peak with four partially resolved hyperfine lines is observed at approximately

320 mT for the film with Y(III) and Cu(II) ions. The e.s.r. data of the spectrum obtained for the film containing Y(III) and Cu(II) ions are  $g_{\perp} = 2.06$ ,  $g_{\parallel} = 2.32$ , and  $A_{\parallel} = 14.0$ . Both of the  $g$ -values decrease and approach 2.0 with the addition of Y(III) ion at  $[Y]/[Cu] = 0.33$ . The peak at  $\sim 320$  mT becomes isotropic in shape with the addition of Ba(II) ions at  $[Ba]/[Cu] = 0.67$ . The addition of Y(III) ions changes the structure of the mononuclear Cu(II) complex, while the latter disappears with the addition of Ba(II) ions. The binuclear Cu(II) complex disappears with the addition of Y(III) and/or Ba(II) ions.

*Figure 5* shows i.r. spectra of the films containing Y(III) and/or Ba(II) ions; the spectrum of the PVA-Cu(II) film with propionic acid is also shown in this figure. The PVA-Cu(II) film has sharp peaks at 1610 and 680 cm<sup>-1</sup>, which are characteristic bands of the carboxylate ion. The intensities of these peaks decrease and the small absorption at 1140 cm<sup>-1</sup> disappears with the addition of Y(III) and/or Ba(II) ions. The addition of the Ba(II) ion results in the appearance of a peak at 1340 cm<sup>-1</sup>. The absorption at 1140 cm<sup>-1</sup> is caused by the crystallization-sensitive band of PVA, while the band at 1340 cm<sup>-1</sup> results from the hydroxy group on the primary alcohol. From these results, it can be seen that the crystal structure of the PVA disappears while the carboxylate ion decreases with the addition of Y(III) and/or Ba(II) ions. The amount of the coordinated hydroxy group increases by the presence of the coexisting Ba(II) and Cu(II) ions.

In the <sup>1</sup>H n.m.r. study of the PVA-Cu(II) film, two acetate groups linked to the Cu(II) ion have been detected<sup>2</sup>. A <sup>1</sup>H n.m.r. study of PVA-Cu(II) films with coexisting Y(III) and/or Ba(II) ions was carried out in order to confirm the existence of acetate groups coordinated with Cu(II) ions. The <sup>1</sup>H n.m.r. spectra of D<sub>2</sub>O solutions of the films were almost identical to that of PVA films. The coordinated acetate group in the PVA-Cu(II) films disappeared with the addition of Y(III) and/or Ba(II) ions.

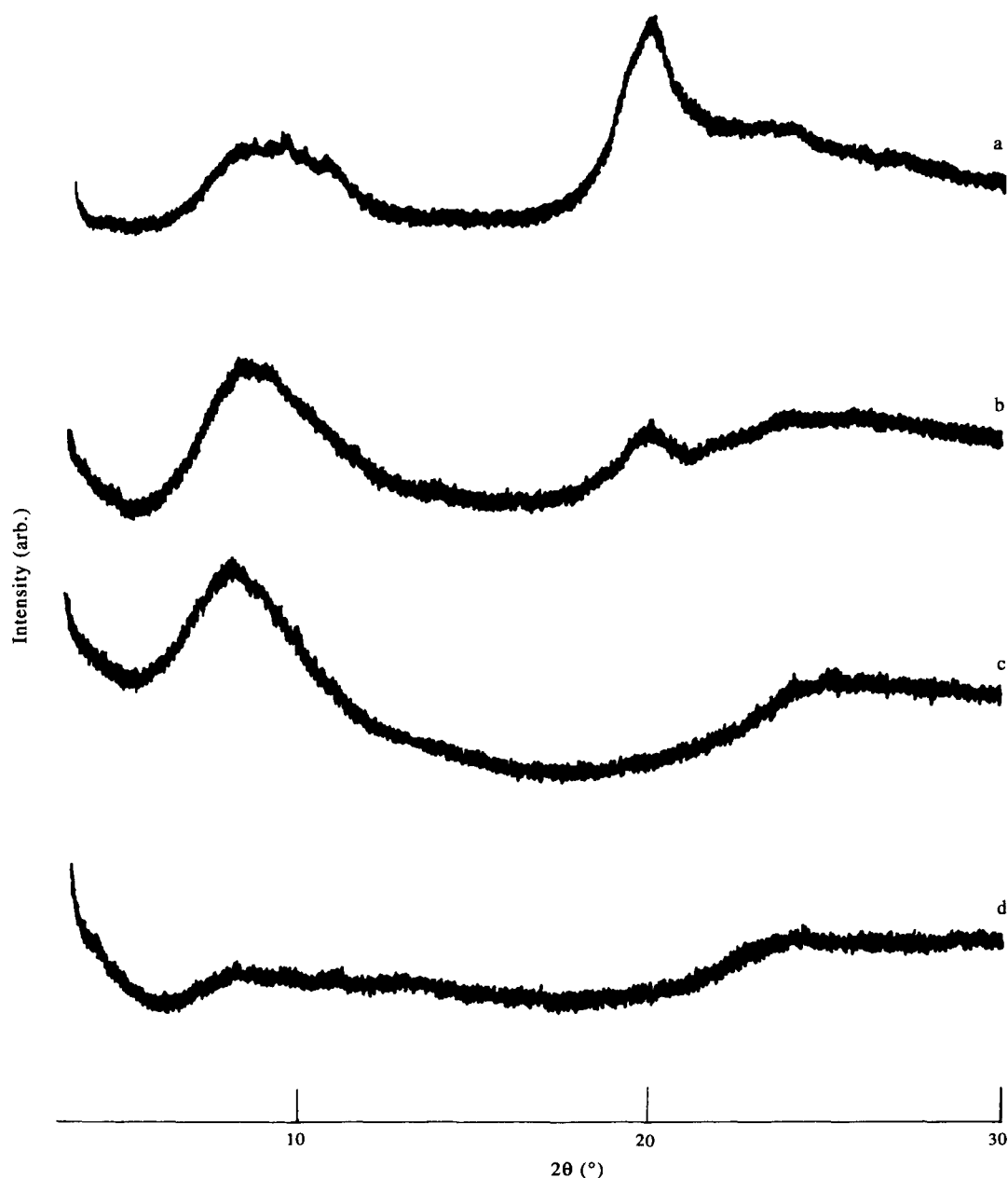


**Figure 7** The relationship between the reduced intensity of absorbance at 700 and 370 nm and the molar ratio of the Cu(II) ion to PVA in films cast from solutions containing 2 mol l<sup>-1</sup> PVA and mixed acetates, where  $[Y]:[Ba]:[Cu] = 1:2:3$ , adjusted to pH 4.3 by adding propionic acid: (○) 700 nm; (△) 370 nm

X-ray diffraction patterns of the films were measured, and these are shown in Figure 6. The PVA film had a sharp peak at  $2\theta = 20^\circ$  which arises from a [101] reflection of the crystal structure resulting from hydrogen bonding of the hydroxy groups<sup>2</sup>. The peak at  $2\theta = 20^\circ$  broadens and other peaks appear with the addition of Y(III), Ba(II) and Cu(II) ions. A pattern with peaks at  $2\theta = 7, 10$  and  $14^\circ$ , due to the Cu(II)-PVA complex structure, is observed for the PVA-Cu(II) films. For the PVA film with Y(III) ions, one broad peak appears at  $2\theta = 9^\circ$ . Three broad peaks at  $2\theta = 8, 11$  and  $25^\circ$  appear for the PVA-Ba(II) films. The addition of these ions breaks up the hydrogen bonding of the PVA, forming new structures with Y(III) or Ba(II) ions complexing with PVA. The position of the peaks for the films with coexisting Y(III) and Cu(II) ions agrees for

the most part with those of the PVA-Cu(II) film (Figures 6a and d), with the pattern of the film with coexisting Ba(II) and Cu(II) ions being only slightly similar to that of the PVA-Ba(II) film. Thus, the Cu(II)-PVA complex still remains in the system where the PVA-Cu(II) film coexists with Y(III) ions. However, the addition of Ba(II) ions affects the Cu(II) ion and leads to the disappearance of the Cu(II)-PVA complex.

It is well known that a metal ion with a small ionic radius and a large positive electric charge tends to form a stable hydroxide complex. The values of the ionic radii for the metal ions considered in this study are  $Y^{+3} = 9.3$ ,  $Ba^{+2} = 13.5$  and  $Cu^{+2} = 7.2$  nm; the order of stability of the complexes are considered to be  $Ba^{+2} < Cu^{+2} < Y^{+3}$ . This suggests that the hydroxy group in PVA coordinates with the Y(III) rather than with the Cu(II) ion, and this is



**Figure 8** X-ray diffraction patterns ( $CuK\alpha$  radiation) for films cast from solutions containing  $2\text{ mol l}^{-1}$  PVA and mixed acetates, where  $[Y]:[Ba]:[Cu] = 1:2:3$ , adjusted to pH 4.3 by adding propionic acid: (a)  $[Cu]/[OH] = 0.053$ ; (b)  $[Cu]/[OH] = 0.11$ ; (c)  $[Cu]/[OH] = 0.22$ ; (d)  $[Cu]/[OH] = 0.30$

followed by the formation of the Cu(II)–PVA complex. Meanwhile, the metal with the lowest electronegativity shows a tendency to donate electrons, and a change in electronegativity between the two atoms is brought about through the formation of an ionic bond. The Pauling electronegativity values for the atoms being considered here are Y = 1.2, Ba = 0.9 and Cu = 1.9. Accordingly, the Ba(II) and Cu(II) ions bond together, and a polynuclear complex containing a metallic cluster of Ba(II) and Cu(II) ions is formed. However, it was not possible to obtain a detailed structure of this complex from these measurements.

Regarding the preparation of the casting solution, the solubility of the copper (II) acetate was increased in the aqueous PVA solution by the addition of yttrium acetate and barium acetate and attained its maximum level at a molar ratio of [Y]:[Ba]:[Cu] = 1:2:3. A homogenous film was obtained by casting from a solution where [Cu]/[OH] > 0.3, but the film produced from an aqueous solution containing PVA and copper (II) acetate also led to the precipitation of the acetate at levels of [Cu]/[OH] > 0.11.

When we consider the u.v./vis spectra of the films with various contents of Y(III), Ba(II) and Cu(II) ions, where [Y]:[Ba]:[Cu] = 1:2:3, there are two absorption bands at 700 and 370 nm, as shown in *Figure 2*. The relationship between the reduced intensity of the absorbance at 700 and 370 nm, and the Cu(II) ion content at a ratio of [Y]:[Ba]:[Cu] = 1:2:3 is shown in *Figure 7*, where the Cu(II) ion content is expressed as a molar ratio of the Cu(II) ion to PVA ([Cu]/[OH]). Maximum values are observed at [Cu]/[OH] = 0.25, showing that the amounts of the mononuclear and binuclear Cu(II)–PVA complexes in the film reach a maximum at this concentration. While the intensities of the films without Y(III) and Ba(II) ions at [Cu]/[OH] = 0.11 are 35 mm<sup>-1</sup> at 700 nm and 10 mm<sup>-1</sup> at 370 nm, as shown in *Figure 3*, both intensities are decreased by the presence of coexisting Y(III), Ba(II) and Cu(II) ions. These decreases are considered to result from the formation of a polynuclear complex containing Y(III), Ba(II) and Cu(II) ions.

*Figure 8* shows X-ray diffraction patterns of the films. The intensity of the peak at  $2\theta = 20^\circ$  weakens and one broad peak at  $2\theta = 8^\circ$  appears as a result of the coexisting Y(III), Ba(II) and Cu(II) ions at a ratio of [Y]:[Ba]:[Cu] = 1:2:3. A maximum intensity of the peak at  $2\theta = 8^\circ$  is observed at [Cu]/[OH] = 0.2. The crystal structure of PVA disappears on increasing the content of these ions, with the hydrogen bonding in the PVA being broken up by the formation of a polynuclear complex with the Y(III), Ba(II) and Cu(II) ions. The precipitation of individual acetates is not observed, even at high concentrations ([Cu]/[OH] = 0.3), and an amorphous structure is formed in the Y–Ba–Cu–PVA film.

The formation of the linear complex is essential for preparation of the precursor Y<sub>1</sub>Ba<sub>2</sub>Cu<sub>3</sub>O<sub>x</sub> filament. The

homogeneous spinning dope system of PVA with a large quantity of metal ions should prove beneficial in the generation of the superconducting phase by heat treatment.

## CONCLUSIONS

In basic research on the solution spinning of Y–Ba–Cu oxide superconducting systems, the Cu(II)–PVA complex structure in the solid state was investigated by using e.s.r. spectroscopy. Both a mononuclear Cu(II) complex and a binuclear Cu(II) complex of the cupric acetate type were found in the film cast from aqueous solutions of PVA and copper(II) acetate.

The influence of Y(III) and Ba(II) ions on the Cu(II)–PVA complexes was examined. While the Cu(II)–PVA complex still remained in systems where the PVA–Cu(II) film coexisted with Y(III) ions, the presence of Ba(II) ions made the Cu(II)–PVA complex disappear. Polynuclear complexes containing Y(III), Ba(II) and Cu(II) ions were formed. A higher solubility of the copper(II) acetate in aqueous PVA solutions was observed by adding yttrium acetate and barium acetate, with the solubility reaching a maximum at a molar ratio of [Y]:[Ba]:[Cu] = 1:2:3. The homogeneous spinning dope system which contained a large amount of these metal ions should prove beneficial in the generation of the superconducting phase by heat treatment.

## ACKNOWLEDGEMENT

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