

SOL-GEL PROCESS FOR PREPARING  $YBa_2Cu_4O_8$  PRECURSORS FROM Y, Ba,  
AND Cu ACIDIC ACETATES/AMMONIA/ASCORBIC ACID SYSTEMS\*

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**Abstract**

Sols were prepared by addition of ammonia to acidic acetate solutions of  $\text{Y}^{3+}$ ,  $\text{Ba}^{2+}$ , and  $\text{Cu}^{2+}$ . Ascorbic acid was added to a part of the sol. The resultant sols were gelled to a shard, a film, or microspheres by evaporation at 60°C or by extraction of water from drops of emulsion suspended in 2-ethylhexanol-1. Addition of ethanol to the sols facilitated the formation of gel films, fabricated by a dipping technique, on glass or silver substrates. At 100°C, gels that were formed in the presence of ascorbic acid were perfectly amorphous, in contrast to the crystalline acetate gels. Conversion of the amorphous ascorbate gels to final products was easier than for the acetate gels. The quality of coatings prepared from ascorbate gels was superior to that of acetate gel coatings.

## 1. Introduction

Numerous papers have covered preparation of the  $\text{YBa}_2\text{Cu}_3\text{O}_x$  (123) phase by sol-gel processes; only a few have been devoted to synthesis of the  $\text{YBa}_2\text{Cu}_4\text{O}_8$  (124) phase by this method. For example, the ammonia/acetate method developed for 123 by Fujihara et al. [1] was modified by Kozuka et al. [2] by adding tartaric acid. They obtained pure 124 phase by heating gel powders at  $780^\circ\text{C}$  for 30 h in flowing  $\text{O}_2$  at 1 atm. In contrast, synthesis of 124 by solid-state reactions generally requires high pressures [3]; at ambient pressure, reactions are incomplete [4,5] or heat treatments of several days are needed [6,7]. Partial-vacuum decomposition of  $\text{BaCO}_3$  at  $750^\circ\text{C}$  promotes more complete synthesis in ambient-pressure  $\text{O}_2$  [8]. The disadvantages of solid-state mixed-oxide methods can be overcome in other variants of sol-gel processing, e.g., by starting from alkoxides [9].

The objective of this study was to apply a modified acetate/ammonia sol-gel process, which has been used by the authors for 123 preparation [10], to prepare 124. The modification consists of introducing a strong complexing agent—ascorbic acid—to the sol. We have found that during synthesis of  $(\text{Bi},\text{Pb})_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_x$  precursors [11,12], this additive promotes formation of homogeneous gels that can be calcined in air directly, without melting, to form carbonate-free ceramics.

## 2. Experiments

A flowchart of the preparation of acetate (AC) and acetate-ascorbate (ASC) sols is shown in Fig. 1. Parameters for gelation to shards, medium-sized microspheres (according to the IChTJ process [13,14]), and coatings (by a dipping technique [15]) are shown in this diagram.

Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) data were obtained with a Hungarian MOM Derivatograph. The products from thermal treatment of the gels were characterized by X-ray diffraction (XRD) measurements (Positional Sensitive Detector, Ital Structure) and infrared (IR) spectroscopy (Perkin Elmer Model 983). For the IR, use of potassium volatiles retained the colours [16].

### **3. Results and discussion**

Thermal analyses of ground AC and ASC gels are shown in Fig. 2. In the AC gels, the thermal transformations are very distinct. The first endotherm, at approximately 300°C, is accompanied by drastic mass loss, presumably from volatiles and chemically combined water. The last sharp exotherm, connected with oxidation of organics, has a maximum at approximately 500°C. The mass of the AC sample is constant from 500 to 930°C. Thermal decomposition of ASC gels is more complex. After a broad endotherm at approximately 150°C, which is associated with a relatively small mass loss, several broad exotherms accompanied by continuous mass losses are observed. The total mass loss for ASC gels was 10% higher than for the AC gels because of the higher organic content. At high temperatures, small reductions in the TGA data indicate reduction of Cu species and loss of oxygen.

The differences between the AC and ASC gels appear to be connected with the extent to which they are amorphous (Fig. 3). After drying at 100°C, the ASC gel is perfectly amorphous, in contrast to the AC gel in which crystalline acetates are observed. The amorphous nature of the ASC gels, in which a strong bidentate network of ascorbic anions is present, seems to be responsible

for the strong bonding of volatiles and the concomitant prolonged thermal decomposition.

The amorphous character of the ASC gels also appears to be responsible for the better coating quality (Fig. 4). In every case [15], it has been confirmed that addition of ethanol to the sols facilitates formation of uniform coatings. Coating thickness decreases with the amount of ethanol added (Fig. 5) and with increased withdrawal rate (Fig. 6). The thickness of the 124 coatings varied from 40 to 20  $\mu\text{m}$  and was greater when glass substrates were used. Representative microspheres of the AC gels are shown in Fig. 7.

In contrast to the AC system, gelation of ASC sol emulsions in 2-ethylhexanol-1 by extraction of water proved unsuccessful. A possible reason is the strong bonding of water to the ASC gel, as reported above.

After calcination of both gels in  $\text{O}_2$  at 450°C for 4 h, the  $\text{CO}_3$  contents were 22% and 19.5% for AC and ASC, respectively. This suggests that some of the carbonates are also combined with copper because if all of the barium were combined as  $\text{BaCO}_3$ , the  $\text{CO}_3$  content should be 14.3%. This speculation is confirmed by XRD (Fig. 3).

Unlike the results for  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_x$  and  $(\text{Bi},\text{Pb})_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_x$  ascorbate gels [11,12], only small reductions of  $\text{CO}_3$  content are observed for ascorbate gel relative to those for acetate gels. However, addition of ascorbic acid results in the formation of more homogeneous and amorphous gels, which confirms the observation of Fujihara et al. [1], who noted a similar effect in the presence of tartaric acid.

#### **4. Conclusions**

Addition of ascorbic acid to acetate ammonia sols facilitates the formation of amorphous gels. In contrast to the results for  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_x$  and  $(\text{Bi},\text{Pb})_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_x$  ascorbate gels, addition of ascorbic acid does not significantly influence carbonate content. At 450°C, excess carbonates relative to  $\text{BaCO}_3$  stoichiometry are observed. Film coatings can be prepared from both acetate and ascorbic acid sols. The ascorbate gel coatings are superior, and further improvement is obtained by dilution with ethanol. Attempts to prepare microspheres from ascorbate sols have been unsuccessful to date.

#### **Acknowledgments**

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**Figure Captions**

Fig. 1. Method for preparation of YBCO124 precursors.

Fig. 2. Thermal analysis of YBCO 124 AC and ASC gels dried at 100°C for 12 days.

Fig. 3. XRD patterns of YBCO 124 AC and ASC gels dried at 100°C for 12 days and calcined 450°C for 4 h.

Fig. 4. Microphotographs of coatings of YBCO 124 AC and ASC gels on glass or Ag substrates.

Fig. 5. Thickness of coatings of YBCO 124 ASC gels (calcined at 450°C for 4 h) vs. vol.% of ethanol; withdrawal rate = 5 cm/s.

Fig. 6. Thickness of coatings of YBCO 124 AC and ASC gels (calcined at 450°C for 4 h) vs. withdrawal rate.

Fig. 7. Microspheres of YBCO 124 AC gels calcined at 750°C for 4 h.

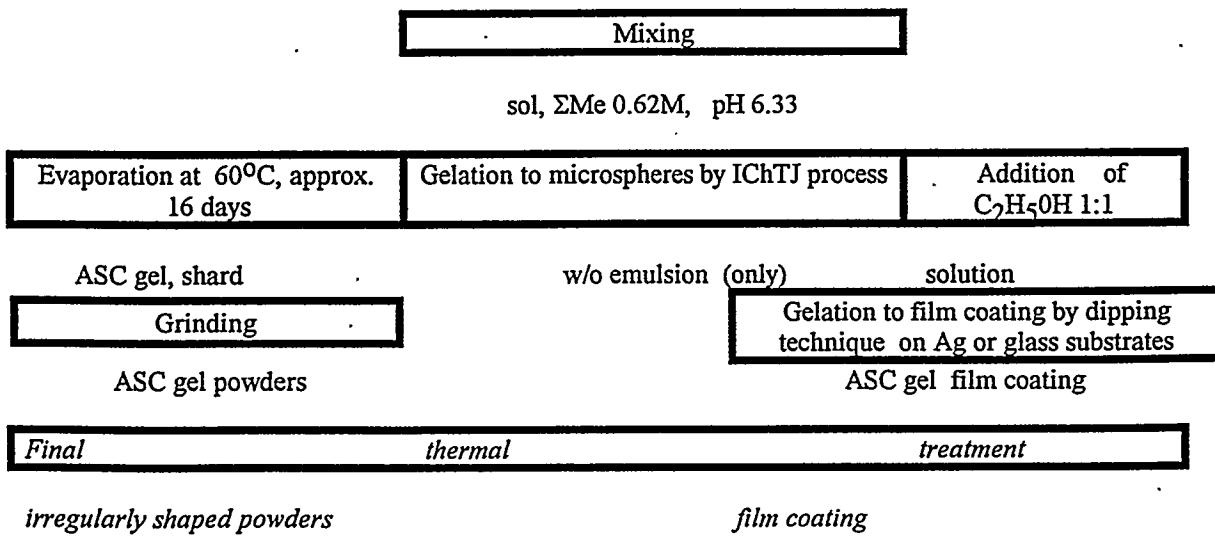
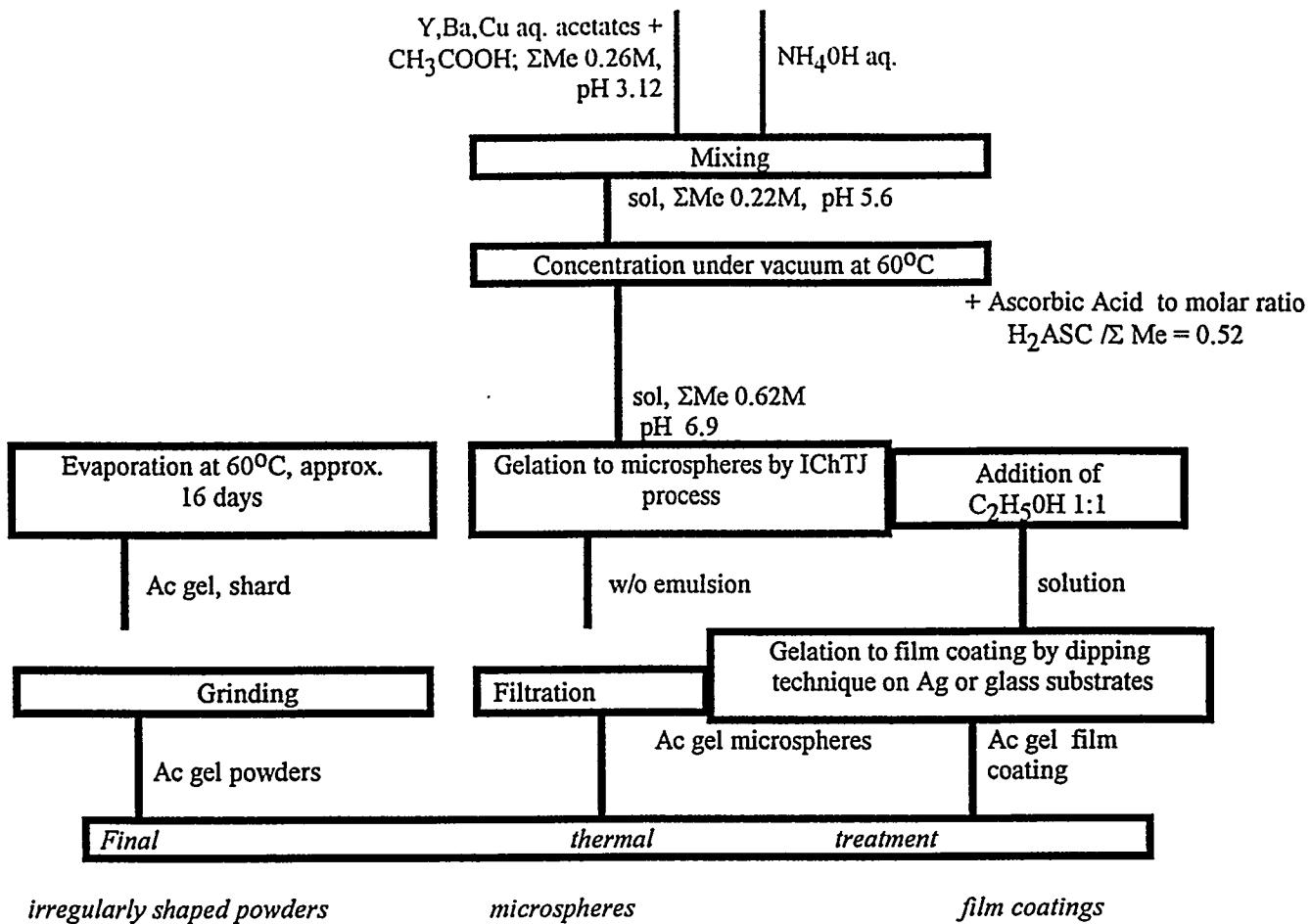


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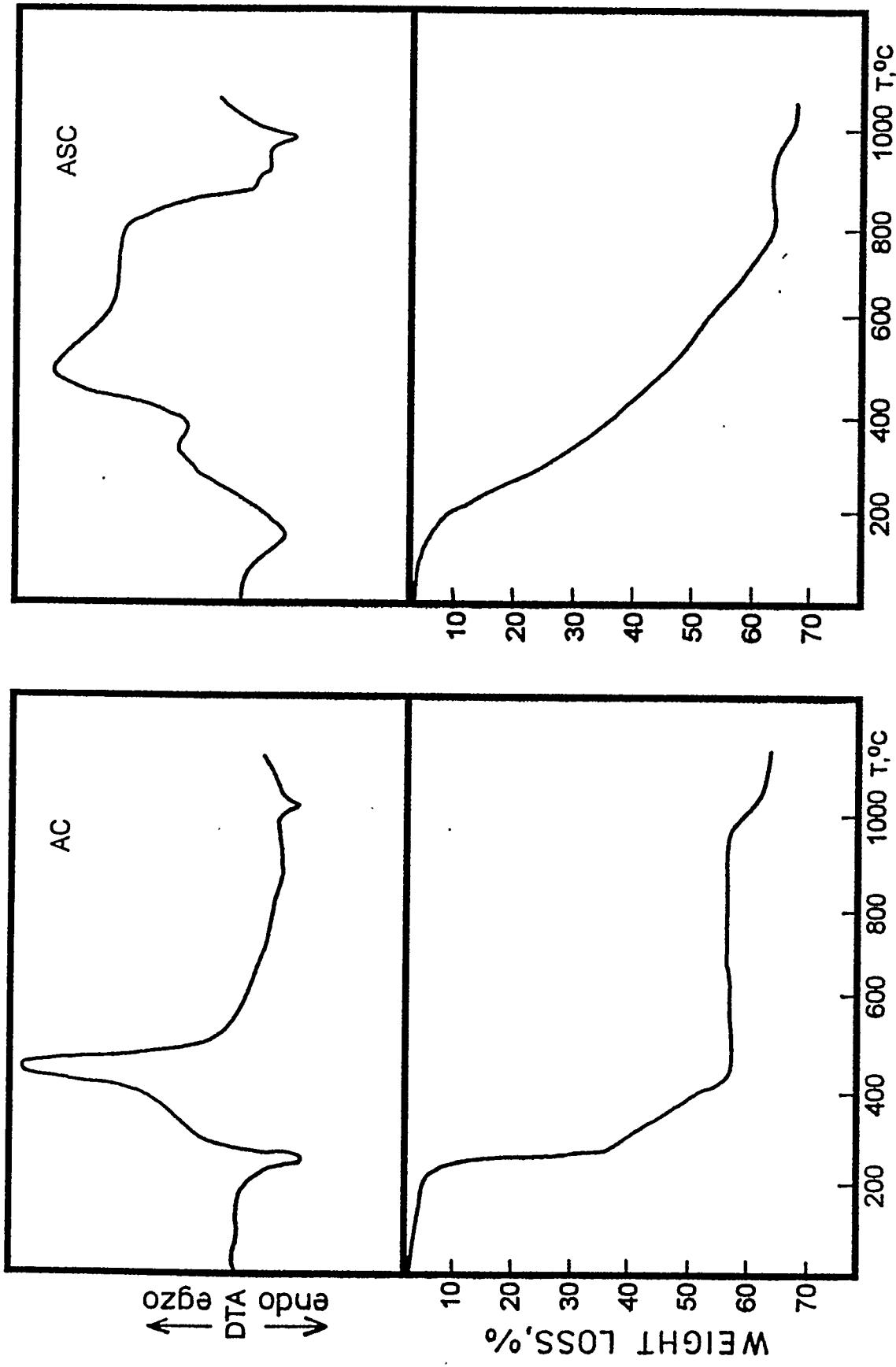


Fig. 2. Thermal analysis of YBCO 124 AC and ASC gels dried at 100°C for 12 days.

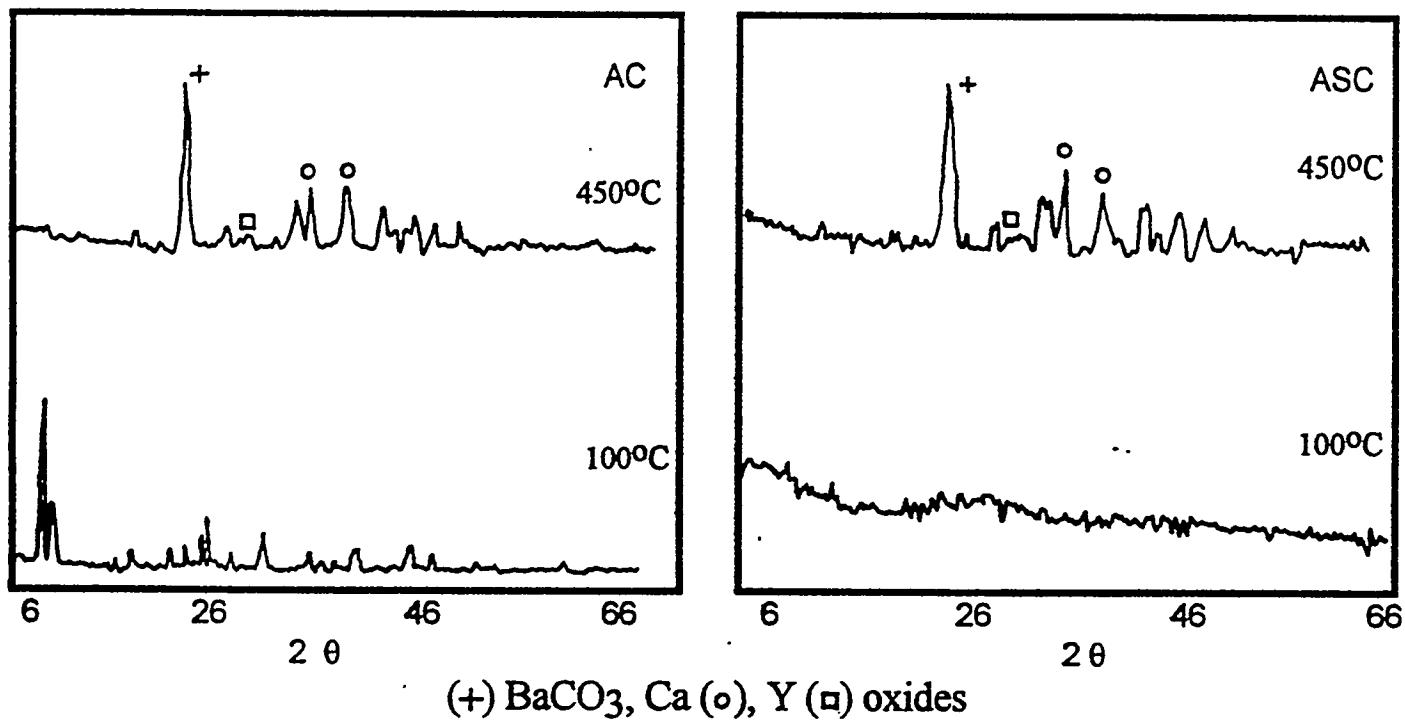
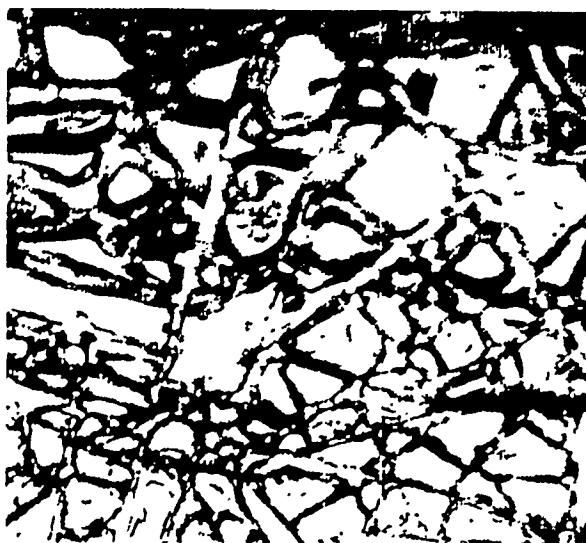


Fig. 3. XRD patterns of YBCO 124 AC and ASC gels dried at 100°C for 12 days and calcined 450°C for 4 h.



1000°C

4h



4500°C

4h

AC

30  $\mu$ m

ASC

Fig. 4. Microphotographs of coatings of YBCO 124 AC and ASC gels on glass or Ag substrates.

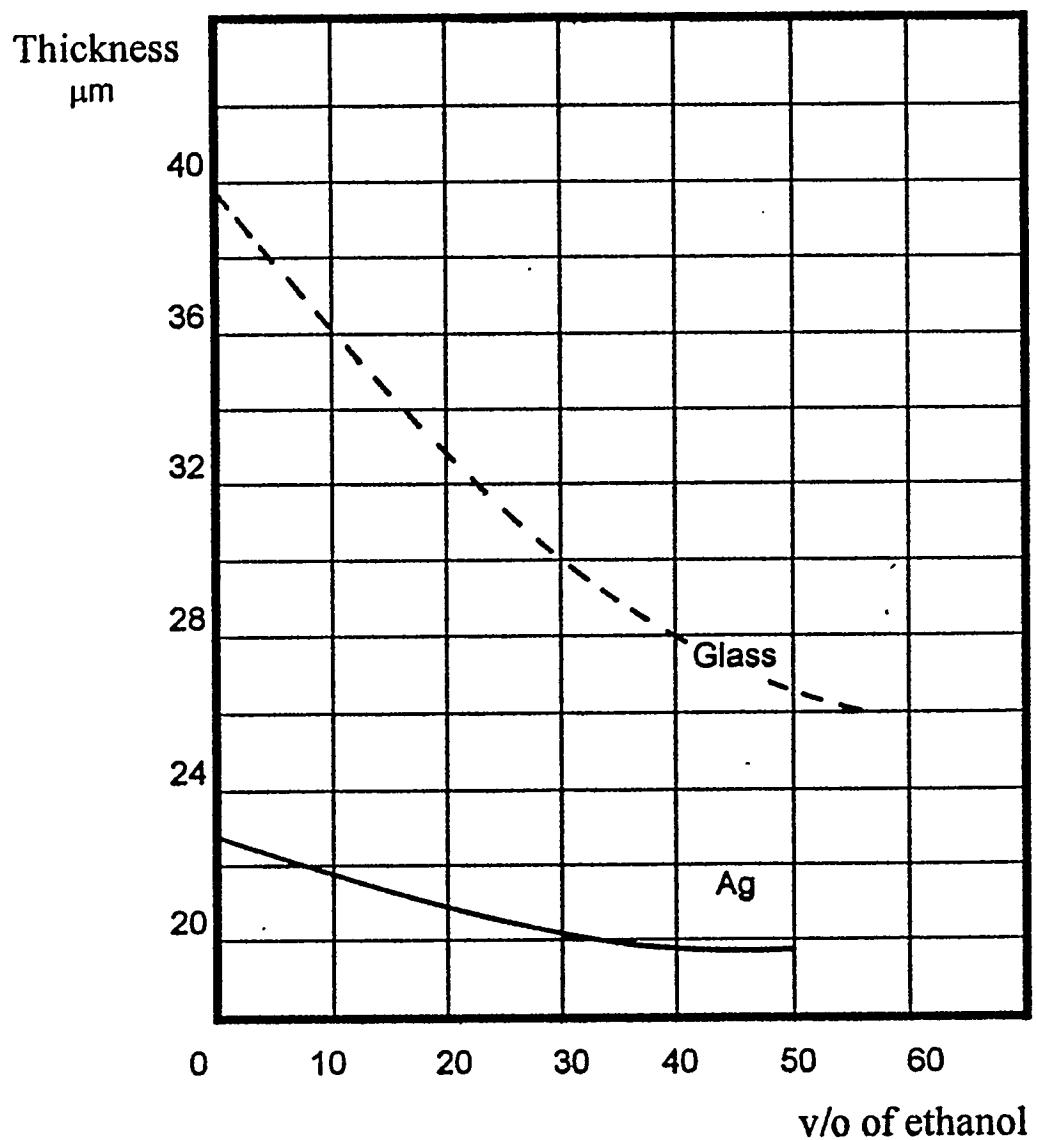


Fig. 5. Thickness of coatings of YBCO 124 ASC gels (calcined at 450°C for 4 h) vs. vol.% of ethanol; withdrawal rate = 5 cm/s.

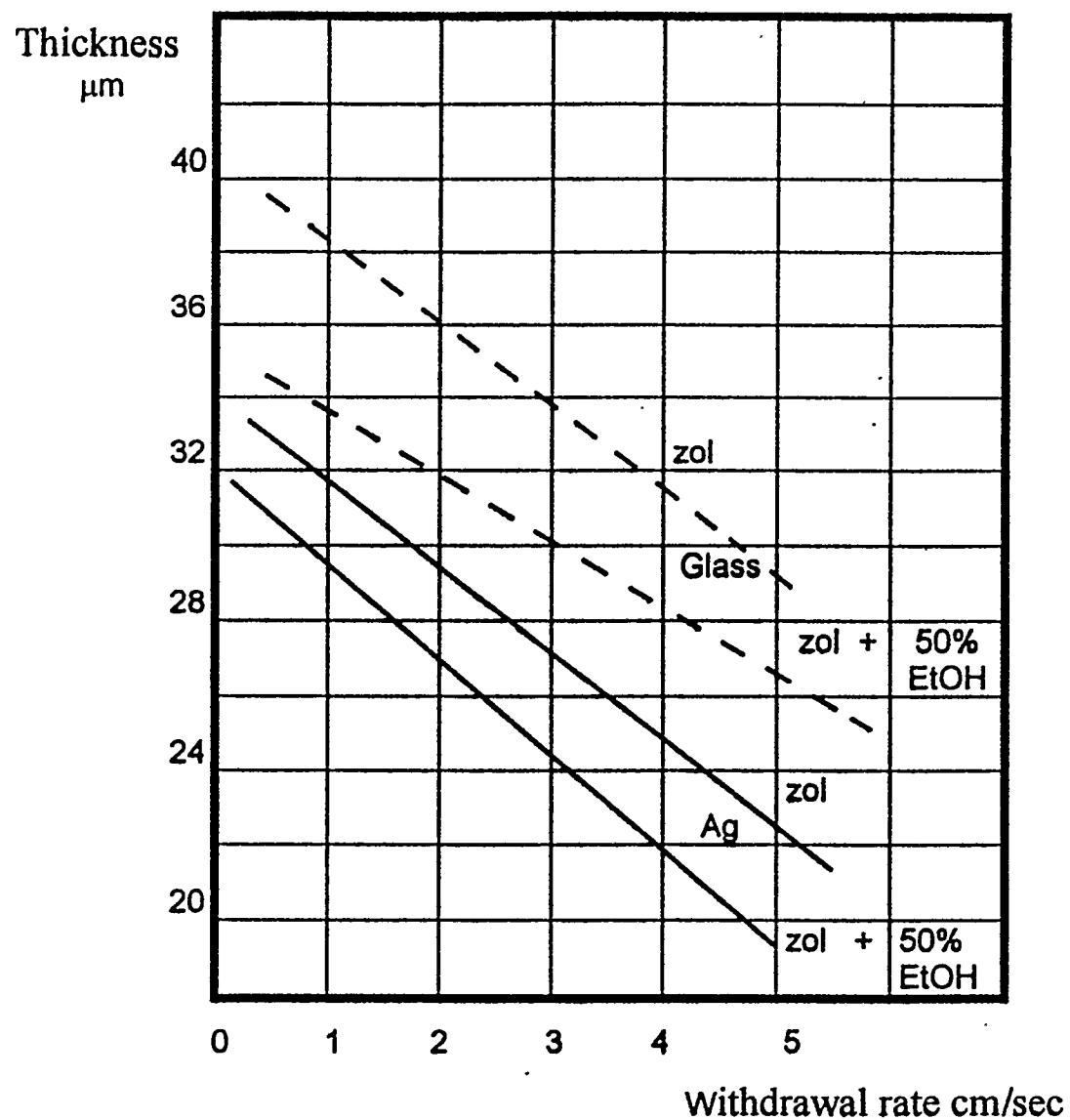


Fig. 6. Thickness of coatings of YBCO 124 AC and ASC gels (calcined at 450°C for 4 h) vs. withdrawal rate.



50  $\mu$ m

Fig. 7. Microspheres of YBCO 124 AC gels calcined at 750°C for 4 h.