SOL-GEL METHOD USED FOR PREPARATION OF THE THIN SUPERCONDUCTIVE LAYERS

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INTRODUCTION

The superconductors with high critical temperature transitions \((HT_c)\) have been attracting much attention since the discovery of perovskite type superconductive oxides by Bednorz and Muller [1]. Several years after their discovery, potential applications are beginning to make their presence felt—even in the job market [2]. The flexible superconductive wires could be utilized in super-powerful magnets, zero resistance electric power transmission and energy storage devices. Superconductive coatings could be used in making special devices such as microwave mixers, magnetoresistors and magnetic sensors.

Superconductive materials are used for the formation of bulks, coatings, fibers and wires. Thin superconductive films have been successfully prepared mainly by physical methods such as sputtering or activated reactive evaporation, which require expensive and specialized apparatus [3]. It is known, that well controlled vapour deposition techniques give oxide films with good transition characteristic [4]. For practical production, however, the methods using solution i.e. wet chemical methods will be advantageous due to their higher productivity.

Material processing has a strong influence on the properties of ceramic superconductors because of the sensitivity of their properties to deviation from optimum stoichiometry and to microstructural heterogeneity such as presence of second phases, porosity, grain boundary segregation etc. [5].

The common method for preparation of the superconductive materials so called dry-powder mix method is based on a solid-state reaction e.g. Y, Ba, Cu oxide or carboxylate powders [6]. The properties of the powder are critical, when this technology is employed. The solid state reaction has slow kinetics, which implies high calcination temperatures and long calcination times. Intermediate grinding can cause product contamination. Finally, there is always possibility, that due to slow kinetics and inhomogeneous mixing the final product contains additional phases.

The calcination temperatures above \(900 \, ^\circ\text{C}\) are still high at these methods, therefore they should be decreased.

The alternative chemical routes, which are originated on the reactions in solution, have been developed to avoid above mentioned problems. The sol-gel technique is the most important representative of these methods. Generally speaking, sol-gel techniques mean all processes, which have as stage of colloidal solution formation (sol formation) as stage of gel formation. The gel or more exactly the precipitate can arise mainly by coagulation processes, i.e. by the powder forming or coprecipitation processes. If the gel is formed by homogeneous solidification of the sol then it is spoken about concentration or metalloorganic methods.

The other important way is the thermal decomposition of inorganic or organic salts corresponding to target oxides. In these methods the product of sol solidification contains the crystalline phase on the contrary to amorphous gel obtained by sol-gel method.

Several superconductive systems such as 
- \(\text{Bi/Cu/Sr/Cu/O, Bi/Pb/Sr/Ca/Cu/O, Y/ Ba/Cu/O, Ti/Ca/Ba/Cu/O, La/M/Cu/O (M = Ca, Sr, Ba)}\) have been prepared by the wet chemical methods [7].

This paper deals with the preparation of the superconductive thin layers by some wet chemical routes. The principles, starting materials, advantages and problems of the methods are discussed.

COATING PROCEDURE

Special techniques are used for the preparation of the thin layers by using of sol solution. At the most frequently utilized method – dip coating process [8], the substrate is dipped into a sol, slowly withdrawn (the withdrawn rates are 3–20 cm/min). Sol should have a sufficient concentration of groups, which are able to fix the originated liquid layer to the surface. The gravitational draining, solvent evaporation and gelation take place at the withdrawing stage [6]. The film thickness depends on the concentration of the
solution, its viscosity and the withdrawal rate. In the case of formation too thick film in one dipping, the adhesion of film to the substrate can be lower, than the forces caused by volume changes of the film during its drying [6]. Film then peels off the substrate. The maximal thickness of the film produced in one step of the dip coating technique might be about 0.5 µm, although some papers have shown the possibility of preparation of film with the thickness about 1 µm [8]. Therefore the films with greater thicknesses are prepared by the repetition of the dipping and film firing.

The second important method is spin coating technique [9]. At this method a small portion of sol is dropped onto the substrate, which rotates (usually about 3000 rpm). The thin films (usually several nm) are prepared by this method.

The third frequently utilized method is the dripping method, based on the putting of the alkoxyde solution in several drops on the substrates [10].

**COPRECIPITATION METHODS**

This group includes the oxalate, carbonate and hydroxide methods. There are some difficulties like non-uniform and incomplete precipitation, contamination by precipitating agents, material loss during precipitation and washing encountered in the methods.

**Oxalate method**

Ammonium oxalate [11], oxalic acid [12] or ethylammonium oxalate [13] added to the aqueous solution of starting chlorides have been used as the precipitating agents. The pH of the solution about 4 has to be kept. The precipitate is filtered and washed.

If the nitrates are utilized as the raw materials the cloudy colloidal solution arises, when the oxalic acid is added. After evaporation of water the gel is obtained [12]. Since the homogeneous gel arises, this route should be classed to concentration processes.

Gel or precipitate is fired at about 300 °C. Porous matrix material is gained by the firing process, which is ground to prepare a powder. The powder can be utilized for preparation of thin films by using of physical methods or treated to a paste. The paste can be used for the preparation of thick film by a screen-printing method [11].

**Carbonate and hydroxide methods**

The procedure used in these methods is analogous to the oxalate technique. The aqueous solution of sodium carbonate has been used as the precipitating agent in the carbonate method [14].

In the hydroxide method, the Y(OH)₃ and Ba(OH)₂ have been used as raw materials and complexing or precipitating agents. The formation of gel or precipitate depends on the character of starting copper compounds. The copper acetate having used, the homogenous gel was formed. The precipitate arises in the case of copper nitrate usage [15].

The above described methods are usually utilized for the preparation of powders or bulk materials although they are, in principle, suitable for layers preparation. There are only a few papers dealing with the layers obtained by these methods [11].

**CONCENTRATION METHODS**

The techniques based on the concentration of sol by the solvent evaporation such as citrate and acetate method can be included to this group. A homogenous gel is formed in these methods. The diluted aqueous solution is used to avoid the uncontrolled partial precipitation. By adding of complexant to the solution and by evaporation of water at elevated temperature, colloidal solution – the sol is gained, which is finally converted to the gel.

**Citrate method**

Citrate route is reported as a simple method, which leads to highly reactive, homogenous submicron – size particles in a relatively short processing time [16–18]. The starting metal-nitrates are dissolved in water. In the most cases, mixture of water and ethylene glycol has been used, which increases the product homogeneity [19]. The solution is mixed with the aqueous solution of citric acid. The following step of addition of the ammonium hydroxide is included to raise pH value above 5. By this way the formation of more stable citrate complexes is supported [20]. The transition of sol to gel by evaporation of water is fast enough to avoid the segregation of the phases [19]. The gel needs to be very slowly decomposed by rising temperature above 300°C to prepare the powder.

Citrate process could be modified by using ethylene diamine – tetraacetic acid (EDTA) as a complexing agent [19]. This technique is of interest for those systems, where no citrate exists. EDTA binds with most metallic elements of periodic table, therefore this method is easily adapted to prepare new types of HTc superconductors.

There are no papers dealing with the preparation of the thick films by using both dip and spin coating methods and citrate route, although the Kozuka stated this possibility [21]. Usually the films are prepared from the powder paste [11].

**Acetate method**

Homogenous gel of the HTc system can be obtained from the aqueous solutions of metal acetates containing acetic acid and tartaric acid. The gel arises after rising of pH solution to 6 by ammonium hydroxide and following evaporation of solvent at the ambient temperature [22]. By dripping the metal acetate
sol onto ceramic substrate superconductive films were prepared [22–24].

The acetate ions play an important role in gel formation – bridging between metal cations through the two electrically negative oxygen of COO group [11]. Tartaric acid was found to be also effective in gel formation, especially in preventing of the crystallization of Cu acetate hydrate during concentration. The tartrate anions may be considered to contribute to the formation of matrix because of the larger number of the sits, which can be bonded to metal cations on the other carboxylate groups through ionic or hydrogen bonding.

In the case of preparation of the superconductive film it is better to use alkylphenol active agent for increasing wettability of the solution to the substrate [10].

SOL-GEL METHOD FROM METAL-ALKOXIDES

The sol-gel method using alkoxides or metalloorganic route generally offers a lot of advantages for formation of films and fibres. Pure and homogenous material can be prepared by this method, but it includes several preparation steps, which can be critical for the properties of the final material. Besides it, it requires expensive chemical agents. It explains, why this method has not been frequently employed for the fabrication of high Tc materials, when compared with the traditional dry powder-mix methods.

The using alkoxides as the raw materials for the preparation of superconductive materials generally offers possibility of films and fibbers formation by easy control of the solution viscosity, as well as high homogeneity, high purity and lower temperature processing [14].

The greatest difficulty of alkoxide method lies in the preparation of a stable sol. The use of cupric organometallic compounds as starting materials is limited by their low solubility in common organic solvents (alcohols, ethers and hydrocarbons-aliphatic or aromatic). Pyridine and acetylacetonate slightly dissolve copper alkoxide, but the obtained concentration is not sufficient for the preparation of coating [25].

Carboxylic acids (such as acetic acid) dissolve the copper alkoxide, but they dissolve also Y/Bar/Cu/O phase and can not be used as a solvent, when repeated application of sol and therefore the greater film thicknesses are required [26].

Alcohol solution of amines, especially alkanolamines dissolve both the copper alkoxide and yttrium alkoxide. The amine alcohol solution does not dissolve the product, making it possible to increase the film thickness by repetition of the coating procedure. Alkanolamines are known to coordinate metal atoms in solution. However amines except of mono, di, tri ethanolamine make yttrium alkoxide to be gelled and cannot be used for obtaining a homogenous solution [27].

Copper acetylacetonate and copper acetate are soluble in alcohol but in the solutions with Ba(OR), Y(OR) ligand exchange between Ba or Y alkoxide and Cu derivates proceeds, leading to the formation of insoluble copper alkoxide [27]. Turova [28] has explained the low solubility of copper alkoxides by the existence of a very strong donor-acceptor bond (see schema).

\[ RO\underset{Cu}{\text{\leftrightarrow}}\text{O}Cu\text{R} \]

The above mentioned facts on copper alkoxides solubility are summarised in the Table I.

The problem of solubility of copper derivates can be solved by several ways.

1) Using of buthylalcohol as the solvent

\[ \text{Cu}(n\text{-OBu})_2 \text{ can be dissolved in buthylalcohol till small concentration (1–2%). Shibata et al. [7, 29] have prepared superconductive Y/Ba/Cu/O powders from metal alkoxides using buthylalcohol as a solvent. The powder was used for preparation of pellets or thick films by painting.} \]

2) Utilizing of acetate or acetylacetonate copper derivates

\[ \text{Cu} (\text{OC}_2\text{H}_4\text{OR})_2 \text{R = Me, Et or Cu(acac)}_2 \text{ can be dissolved in absolute 2-ethoxy or 2-methoxyethanol with vigorous stirring. The reason of increased solubility of these copper substances in comparison with the copper alkoxides is formation of chelates soluble in organic solvents [28–32].} \]

3) Increasing of copper alkoxide solubility by adding of ethanolamine

Copper alkoxides are soluble in alcohol or alcohol-hydrocarbons mixtures with ethanolamine. The high basicity of a nitrogen atom in triethanolamine may produce partially or completely amine-coordinate copper, which makes the copper alkoxide to be soluble in solution [21].

This method is useful for Y/Ba/Cu/O and Bi/Ca/Sr/Cu/O system. In the case of Y/Ba/Cu/O system, there is a problem with solubility Y(OR)_3 in solvent. The best solvents are hydrocarbons, another possibility is dissolving Y(n-butoxide) in mixture of methanol and triethanolamine [26]. Resultant solution is coated on the substrate by dripping or dipping method [8].

By addition alkanolamines to the solvent (diethanolamine:alkoxide = 1:1) the concentrated solution of mixed alkoxide without precipitation of any solid phase can be prepared [8]. Moreover, hydrolytic reaction is strongly suppressed and kept to a mild rate by the addition of alkanolamines to the solution.
Table I

Solubility of copper alkoxides in various organic solvents

<table>
<thead>
<tr>
<th>Solvent</th>
<th>H₂O</th>
<th>Cu(OEt)</th>
<th>Cu(i-OPr)</th>
<th>Cu(n-OBu)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetic Acid</td>
<td>o</td>
<td>o</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>Acetone</td>
<td>o</td>
<td>x</td>
<td>o</td>
<td>o</td>
</tr>
<tr>
<td>Diethanolamine+Ethanol</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
</tr>
<tr>
<td>2-Dimethylamino-ethanol</td>
<td>o</td>
<td>x</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>N,N-Dimethylform-amide</td>
<td>o</td>
<td>*</td>
<td>*</td>
<td>*</td>
</tr>
<tr>
<td>2-Ethoxyethanol</td>
<td>o</td>
<td>x</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>Ethylenediamine</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
</tr>
<tr>
<td>Formamide</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
</tr>
<tr>
<td>2-Methoxyethanol</td>
<td>o</td>
<td>x</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>Propionic Acid</td>
<td>o</td>
<td>*</td>
<td>o</td>
<td>o</td>
</tr>
<tr>
<td>Pyridine</td>
<td>o</td>
<td>x</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>Triethanolamine+Ethanol</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
</tr>
<tr>
<td>Acetylaceton</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>Chloroform</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>Hexane</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>Toluene</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>Xylene</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
</tr>
</tbody>
</table>

o ... soluble,  * ... sparing soluble, x ... insoluble

Affinity of each solvent to water was checked because of additional hydrolysis reaction.

The solubility of copper alkoxides in various organic solvents is provided in Table I. Thin gel films can be prepared in air by dipping without precipitation of oxide or hydroxide powder, which would otherwise occur due to aggressive hydrolytic reaction.

4) Using of copper nitrates

Maruhami et al. [33, 34] have solved the problem of low solubility of copper alkoxides by their replacement with another copper salt (Cu-nitrate). In this case, the hydrolysis can be hardly controlled, on the contrary to alkoxide. This is the reason why only fine powders were obtained. Cu nitrate, besides of ability to prepare highly concentrated mixed solution, promotes formation of the Ba nitrate, which interrupts the formations of Ba carbonate.

5) Increasing of solubility by using of CO₂

Matsumura et al. [35] reported formation of uniform solutions by reaction of mixture of solvents and Bi, Pb, Sr, Ca, Cu alkoxides with carbon dioxide. The most probable process is reaction of alkoxides with carbon dioxide and insertion of CO₂ between metal and oxygen to form soluble alkyl carbonates.

After being dried, the gel thin films were introduced directly into a furnace, kept at 500 °C to decompose the organic groups in the gel films. About 0.05 µm thick superconductive films can be prepared in one dipping [33]. To increase the thickness of the film it is necessary to repeat the application and heating [5]. Then the film of several µm thick can be obtained.

DECOMPOSITION METHODS

The chemical precursors solutions of metal nitrates, acetates or carboxylates are spread onto substrate. In some cases the hot substrate is employed, which increases the film adhesion to substrate [36]. Finally, a high temperature treatment is needed to convert the precursors to oxides and to induce the formation of the HTc superconductive phase [37]. The main problem encountered in these methods can be a heterogeneous segregation caused by difference in decomposition temperatures of salts [38-41].

Thermal decomposition of metal nitrates

The method can be utilized only in the preparation of coatings. This procedure gives good metallic behaviour and sharper transition than carbon-based precursors, because it excludes the formation of carbonates during the firing.

The poor solubility of salts in ethanol is solved by using of glycerol-water solvent [42]. The smooth films were obtained through spraying [43]. Spray pyrolysis
Sol-gel Method Used for Preparation...

Table II

The influence of substrate material on the $T_c$ of Y/Ba/Cu/O and Bi/Ca/Sr/Cu/O films

<table>
<thead>
<tr>
<th>System</th>
<th>Substrate</th>
<th>Transition temp.</th>
<th>Calcination temp.</th>
<th>Gir</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bi/Ca/Sr/Cu/O</td>
<td>MgO</td>
<td>60-70</td>
<td>875</td>
<td>11</td>
</tr>
<tr>
<td></td>
<td>SrTiO$_3$</td>
<td>70-90</td>
<td>875</td>
<td>37</td>
</tr>
<tr>
<td></td>
<td>ZrO$_2$</td>
<td>77-83</td>
<td>820</td>
<td>41</td>
</tr>
<tr>
<td>Y/Ba/Cu/O</td>
<td>MgO</td>
<td>70-80</td>
<td>800</td>
<td>74</td>
</tr>
<tr>
<td></td>
<td>SrTiO$_3$</td>
<td>55</td>
<td>850</td>
<td>9</td>
</tr>
<tr>
<td></td>
<td>ZrO$_2$</td>
<td>56-98</td>
<td>800</td>
<td>41</td>
</tr>
</tbody>
</table>

is more convenient than another methods, if the uniform and fine droplets are prepared and their thermal decomposition controlled. Films prepared from aqueous-glycerol nitrate solution provide at lower annealing temperature better superconductive properties, than from aqueous-nitrate solutions [43]. Films have been obtained also by ultrasonic spray pyrolysis of aqueous-glycerol solution of Y, Ba, Cu nitrates [43].

Rheological properties of nitrate solutions are not well adapted to dipping. But, some authors reported preparation of Y/Ba/Cu/O films from solution on a hot substrate by the spin coating, dipping or brushing [44, 45]. Sei et al. [75] have used the nitrates dissolved in the glycerol for the preparation of bulk materials and dip coated thin films in the Bi/Sr/Ca/Cu/O system.

**Thermal decomposition of organic acid salts**

This method is very simple, inexpensive, shows higher growth rates of films. It utilizes some organic acid salts or chelate compounds (napthenates, stearates and carboxylates) as a raw material [46-53].

Mixture of salts was dissolved by addition of suitable solvent-toluene [48-50], industrial gasoline [46, 47], chloroform [51], or pyridine [52, 53]. The substrate was coated by dipping, the layer was fired. This cycle was repeated until a desired thickness was achieved. After that, the film was sintered and annealed. Superconductive phase was formed at lower temperature than in conventional solid-state reaction, but $T_c$ were lower [54].

**THERMAL TREATMENT OF FILMS**

The films prepared at above mentioned methods should be thermal treated to induce the superconductive phase. It is known, that the high heat treatment temperatures, especially calcination ones results in the interaction between the substrate and film [55]. This is why, the films with very weak superconductive properties were prepared on SiO$_2$ substrates [5]. To avoid the substrate reaction, the ways as an utilization of less reactive substrate (yttrium stabilized ZrO$_2$ i.e. YSZ, SrTiO$_3$, MgO, Bi/Ca/Sr/Cu/O or Y/Ba/Cu/O materials), formation of buffer layers, lowering of calcination temperature etc. and their combination have been used [14, 52]. The influence of substrate material on the superconducting properties is depicted in the Table II.

Unfortunately the calcination temperatures at all methods employing the carbon containing precursors are still too high. When an attempt was made to decrease this temperature to 800 °C in Y/Ba/Cu/O material obtained by acetate method the semiconducting and non-superconducting product has been found, although superconductive phase was in excess [57-62]. The reason is, that the carbonates especially BaCO$_3$, which can arise at the heating of gel, need the high decomposition temperatures at about 900 °C. A film thicker than 0.8 µm has to be formed in order to be able to observe any superconductivity [8].

Neither the using of nitrate based precursors can solve the problem of substantial lowering of the calcination temperatures. Sei et al. [75] have shown that the calcination temperature 845 °C is necessary for the Bi/Ca/Sr/Cu/O films on YSZ plates to be prepared by using of nitrate sol.

The lowering of heat treatment temperatures of Y/Ba/Cu/O film can be achieved by using of low oxygen partial pressure during the firing of films, followed by annealing in an oxygen flow [52]. The utilization of ozone for the suppressing of formation of intermediate phases such as BaCuO$_2$ and Y$_2$BaCuO$_5$ might be
The influence of calcination temperature on the $T_c$ of films obtained by various methods

<table>
<thead>
<tr>
<th>Preparation method</th>
<th>System</th>
<th>$T_c$ [K]</th>
<th>Calcination temp. [°C]</th>
<th>Cit.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxalate</td>
<td>Bi/Ca/Sr/Cu/O</td>
<td>95</td>
<td>890</td>
<td>[11]</td>
</tr>
<tr>
<td>Citrate</td>
<td>Y/Ba/Cu/O</td>
<td>80</td>
<td>900</td>
<td>[72]</td>
</tr>
<tr>
<td></td>
<td>Bi/Ca/Sr/Cu/O</td>
<td>97</td>
<td>950</td>
<td>[37]</td>
</tr>
<tr>
<td></td>
<td>Ti/Ba/Ca/Cu/O</td>
<td>80</td>
<td>900</td>
<td>[37]</td>
</tr>
<tr>
<td></td>
<td>Pb/Bi/Ca/Sr/Cu/O</td>
<td>105</td>
<td>950</td>
<td>[56]</td>
</tr>
<tr>
<td>Alkoxide</td>
<td>Y/Ba/Cu/O</td>
<td>90</td>
<td>920</td>
<td>[30]</td>
</tr>
<tr>
<td></td>
<td>Bi/Ca/Sr/Cu/O</td>
<td>95</td>
<td>850</td>
<td>[30]</td>
</tr>
<tr>
<td>Alkoxide (Oxygen containing solvents)</td>
<td>Y/Ba/Cu/O</td>
<td>75</td>
<td>950</td>
<td>[74]</td>
</tr>
<tr>
<td></td>
<td>La/Sr/Cu/O</td>
<td>45</td>
<td>900</td>
<td>[74]</td>
</tr>
<tr>
<td></td>
<td>Ti/Ba/Ca/Cu/O</td>
<td>100</td>
<td>900</td>
<td>[69]</td>
</tr>
<tr>
<td></td>
<td>Pb/Bi/Ca/Sr/Cu/O</td>
<td>110</td>
<td>860</td>
<td>[35]</td>
</tr>
<tr>
<td>Alkoxide (Amines)</td>
<td>Y/Ba/Cu/O</td>
<td>88</td>
<td>850</td>
<td>[34]</td>
</tr>
<tr>
<td></td>
<td>Bi/Ca/Sr/Cu/O</td>
<td>98</td>
<td>800</td>
<td>[25]</td>
</tr>
<tr>
<td>Organometallic decomposition</td>
<td>Y/Ba/Cu/O</td>
<td>90</td>
<td>850</td>
<td>[53]</td>
</tr>
<tr>
<td></td>
<td>Pb/Bi/Ca/Sr/Cu/O</td>
<td>107</td>
<td>850</td>
<td>[44]</td>
</tr>
<tr>
<td>Spray pyrolysis</td>
<td>Y/Ba/Cu/O</td>
<td>75</td>
<td>900</td>
<td>[52]</td>
</tr>
<tr>
<td></td>
<td>Bi/Ca/Sr/Cu/O</td>
<td>80</td>
<td>850</td>
<td>[43]</td>
</tr>
<tr>
<td>Acetate</td>
<td>Y/Ba/Cu/O</td>
<td>93</td>
<td>910</td>
<td>[22]</td>
</tr>
<tr>
<td></td>
<td>Bi/Ca/Sr/Cu/O</td>
<td>115</td>
<td>820</td>
<td>[22]</td>
</tr>
<tr>
<td>Solid-state</td>
<td>Y/Ba/Cu/O</td>
<td>90</td>
<td>950</td>
<td>[36]</td>
</tr>
<tr>
<td></td>
<td>Bi/Ca/Sr/Cu/O</td>
<td>110</td>
<td>900</td>
<td>[36]</td>
</tr>
</tbody>
</table>

Another way for the solution of problem of lowering of heat treatment temperatures [27]. Some results of the influence of calcination temperature on the $T_c$ of film are summarized in the Table III [68–71].

CONCLUSIONS

The wet chemical methods have offered the extensive possibilities in the preparation of HTc superconductive materials, especially the powders, fibres and films. The most effective way seems to be the sol-gel method employing alkoxides as starting materials, although the problem of solubility of copper alkoxides has not been solved satisfactorily yet. The homogeneous superconductive phases with no additional phases can be prepared by above mentioned methods. They offer powerful means for the new superconductive materials to be gained. So far neither these methods have proposed the efficient way for the substrate reaction to be suppressed. This is why the superconductive films with lower $T_c$ in comparison with bulk are prepared by these methods.

References


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