

CHARACTERIZATION OF BARIA-ALUMINA-SILICA GLASSES AND $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$
 SUPERCONDUCTING FILMS PREPARED BY THE SOL-GEL-PROCESS
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ABSTRACT

The preparation of eutectics in the system $\text{BaO-Al}_2\text{O}_3\text{-SiO}_2$ by the conventional technique is carried out by fusions with intermittent crushing and grinding. Hydrolysis and polycondensation of alkoxides in a suitable solvent provide a simple way to obtain the homogeneous baria-alumina-silica glasses. The physical and chemical changes which occur during the gel-to-glass conversion were investigated on gel powders by thermal gravimetric analyses, differential thermal analyses, mass spectroscopy, nitrogen sorption analyses, and dilatometry.

By means of the sol-gel route it is also possible to prepare coating solutions in the Y-Ba-Cu-system. Coatings of composition $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ were deposited on substrates using dip coating and characterized by scanning electron microscopy and measurements of superconducting temperature.

INTRODUCTION

The preparation of high melting glasses (melting temperatures remarkably above 1600 °C) leads to practical problems like reaction with the crucible walls. The high temperatures in general are required in order to obtain sufficient homogeneity of the melt. In the system $\text{BaO-Al}_2\text{O}_3\text{-SiO}_2$ the general way is to melt, to crush the melt, to grind and to remelt [1]. Thus, sufficient homogeneity of the glass is obtained, and too high melting temperatures can be avoided. Sol-gel techniques should have general advantages in this case, if sufficient homogeneous gels can be prepared from solutions. Far lower processing temperatures should be possible, since homogeneity can be obtained in solution at room temperature. In ceramics, more homogeneous powders in multicomponent systems offer the possibility of lowering the reaction temperatures compared to mixed oxides, since diffusion paths can be reduced and amorphous starting materials show good sinter activities. For film formation, coatable precursors can be synthesized, too. Especially the film formation is of high interest in some perovskite structures like high temperature superconductors. Therefore, it is necessary to investigate the gel-to-glass or to ceramic phase conversion of these systems.

EXPERIMENTAL RESULTS

Preparation of solutions

Our first investigations of the alkoxide route showed that in the presence of aluminum and barium alkoxides the hydrolysis and condensation reactions of tetraalkoxy silanes resulted usually in the formation of only oligomeric silicic acid esters which evaporated and led to remarkable SiO_2 losses. On the other

hand, the addition of a complexing agent such as ethylacetate to the solution allowed to increase the solubility of the formed metal (oxide)hydroxides and the homogeneity of the sol. Furthermore, the formation of a Si-O-Al bond to prevent binder formation completely. Stable solutions corresponding to the ultimate oxide composition in the range of about 55 wt.% SiO₂, 10 wt.% Al₂O₃, and 35 wt.% BaO were prepared by mixing the adequate amount (for 10 g glass) of aluminum-sec-butoxide dissolved in 100 ml isopropanol and ethylacetate (C₄H₁₀O₂) dissolved in 24 ml isopropanol, according to a molar ratio of Al₂O₃:BaO = 1:1. To the solution 0.73 ml water in 24 ml isopropanol (tetramethylorthosilicate were added dropwise. Finally, the barium (metal reacted with 64 ml methanol) and 400 ml water were added to the solution under intensive stirring. The substitution of barium and aluminum alkoxides by the nitrates was also possible. In that case, the acidification of the aqueous solution impeded the formation of oligomeric silicic acid esters.

The use of alkoxides to prepare solutions in the YBa₂Cu₃O_{7-x} system was limited because the copper alkoxides (of low molecular weight) are polymeric solids and insoluble. In order to obtain solutions corresponding to an oxide composition of YBa₂Cu₃O_{7-x} it was suitable to employ soluble copper complexes as starting materials. 266 mg yttrium(III)isopropoxide, 783 mg copper(II)2,4-pentanedionate, and 274 mg barium were dissolved in 100 ml 2-methoxyethanol, resulting in a clear blue solution which could be used for coating.

Photon correlation spectroscopy

The size distribution of the sol particles was determined by photon correlation spectroscopy (Malvern Automeasure 4700). The mean particle size in the BaO-Al₂O₃-SiO₂ sol was found to be about 470 nm before and 1.5 - 10 μm after water addition. In the YBa₂Cu₃O_{7-x}-system the mean particle size was determined to be about 130 nm.

Spray drying of the BaO-Al₂O₃-SiO₂ sol

BaO-Al₂O₃-SiO₂ gel powders were generated by spray drying (Buchi, 190 Mini Spray) of the sol at 160 °C. The size distribution of the gel powder determined by laser scattering (Malvern, particle sizer 1600) can be expressed by the Rosin-Rammler-Bennett exponential equation,

$$R = 100 \cdot \exp[-d/x]^N, \quad (1)$$

where R is the retention [%] and d the measured particle size. The RRB-coefficients were ascertained to be $x = 5.11 \mu\text{m}$ (mean particle size), and $N = 6.25$ (half width). Nitrogen sorption analyses have shown that the specific surface of 266 m²g⁻¹ is traced back to micropores ($R < 1 \text{ nm}$).

Thermal treatment of BaO-Al₂O₃-SiO₂ gel powders

The physical and chemical changes which occur during the gel-to-glass conversion were investigated by thermal gravimetric

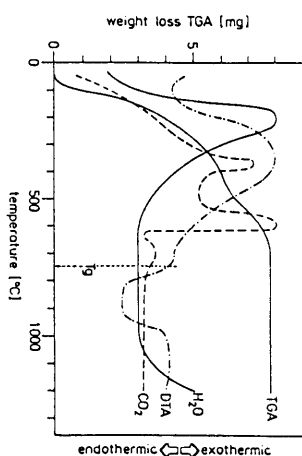


Figure 1. Thermal gravimetric analysis (TGA), differential thermal analysis (DTA), and mass spectroscopy (MS) for the BaO-Al₂O₃-SiO₂ gel powder (45.8 mg). The heating rate was 20 K/min.

analysis (TGA), differential thermal analysis (DTA), and mass spectroscopy (MS). The TGA-DTA-MS curves are shown in Figure 1. Up to 700 °C the weight loss was due to the evaporation of water, solvent and CO₂ gas produced by decomposition of residual organic compounds. The transformation temperature of Tg = 750 °C indicated by shifting of the DTA-base-line corresponds to the value of molten glass of same composition. For temperatures T > 1000 °C melting reactions started due to the large amount of water in the form of OH groups in the system. On the basis of the TGA-DTA-MS curves the following temperature program was used to densify the gel powders: heating rate to 350 °C: 80 K hr⁻¹, interval at 350 °C for 16 hrs, heating rate to 700 °C: at 40 K hr⁻¹, interval at 700 °C for 0.5 hrs, cooling rate to room temperature: 150 K hr⁻¹, in air.

During thermal treatment up to 700 °C the BET surface decreased to 191 m²g⁻¹, and the size of micropores was shifted to larger values R_v = 4 - 8 nm.

The gel-to-glass conversion was achieved by thermal treatment for 5 hrs in oxygen atmosphere at 950 °C with decrease of the specific surface to 3 m²g⁻¹.

Isothermal sintering

Thermal treated gel powder was pressed into a fused silica tube of 5 mm diameter at 0.5 MPa. The linear shrinkage $\epsilon(t)$ as a function of time was determined by means of a dilatometer. In Figure 2 the linear shrinkage $\epsilon = \Delta l/l_0$ of the thermal treated gel powder is shown at different temperatures compared with a conventionally prepared glass powder (diameter $x = 5 \mu\text{m}$).

In the initial phase the velocity of sintering for the thermal treated gel powder was larger than that for the conventionally prepared glass powder.

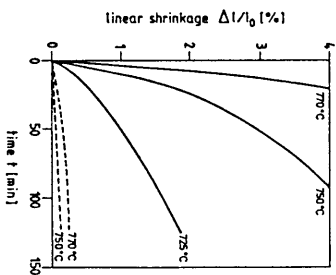


Figure 2. Linear shrinkage of thermal treated gel powder and conventionally prepared glass powder (dashed lines).

Preparation of coatings in the $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ system

Dip coating was used throughout these experiments, since uniform films can be produced. After coating the substrate was allowed to stand in air for completion of hydrolysis by atmospheric moisture, then a heat treatment was required to produce a densified film. The structure of the coating at different temperatures was characterized by X-ray diffraction, shown in Figure 3.

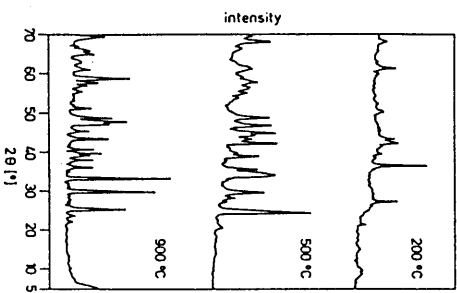


Figure 3. X-ray diffraction pattern for $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ gels densified at 200°C, 500°C, and 900°C.

Up to temperatures of $T \sim 200^\circ\text{C}$ the formation of copper and copper(II) oxide was observed. At higher temperatures of $T \sim 500^\circ\text{C}$ copper(II) oxide, yttrium oxide, barium oxide, and barium carbonate were formed. For temperatures $T > 850^\circ\text{C}$ the tetragonal superconducting phase of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ [2] was obtained. Figure 4 shows SEM micrographs of the deposited films dried at 100°C (a)

and densified at 900°C in oxygen atmosphere (b). The densified layer was very dense and about $1\ \mu\text{m}$ thick. Figure 4b was obtained after scratching the surface with a diamond.

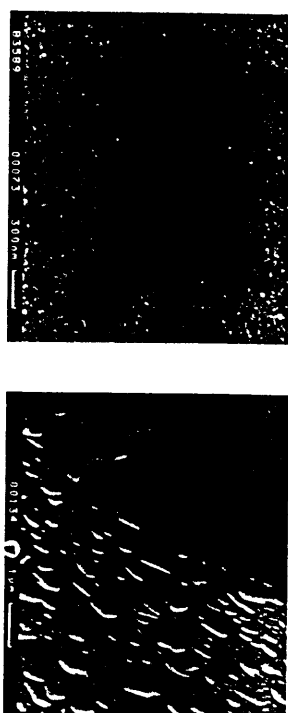


Figure 4. SEM-micrograph of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ -films dried at 100°C (a) and densified at 900°C (b).

DISCUSSION

In order to explain the high velocity of sintering for the $\text{BaO-Al}_2\text{O}_3\text{-SiO}_2$ gel powder it is convenient to apply Frenkel's sintering model [3] to the shrinkage measurements. For the initial phase of sintering:

$$\frac{\Delta l}{l_0} = \frac{3\sigma}{4nR_0} t, \quad (2)$$

where σ is the surface tension, n is the viscosity, and R_0 the radius of the glass particles. For the conventional prepared glass powder the size of glass particles was determined to be $R_0 = 0.68\ \mu\text{m}$, where $\eta/791 = 750^\circ\text{C}$ was determined to be $R_0 d \epsilon/t(\text{Pg}) = 3.3 \cdot 10^{-5}\ \text{s}$. The determined particle size R_0 corresponds to the fine-grained part of the used size distribution. For the thermal treated gel powder a radius $R_0 = 13.5\ \text{nm}$ follows from $\epsilon/t(\text{Pg}) = 1.67 \cdot 10^{-5}\ \text{s}$, corresponding to initial particles which form the spray agglomerates (Figure 5).

The high sintering rate is caused by the colloidal structure of the gel powder. The activation energy of viscous flow Q defined by:

$$\eta = \eta_0 \exp[Q/KT] \quad (3)$$

which was determined to be larger than that for the conventional prepared glass powder. The correlation lengths of cooperative displacement regions are larger for gels. The decrease of the melting temperature of the $\text{BaO-Al}_2\text{O}_3\text{-SiO}_2$ gels is correlated with the large amount of water.

As opposed to vitreous materials the large shrinkage of the gel particles usually leads to the formation of pores in the sintered ceramic. Therefore, reason one main advantage of the sol-

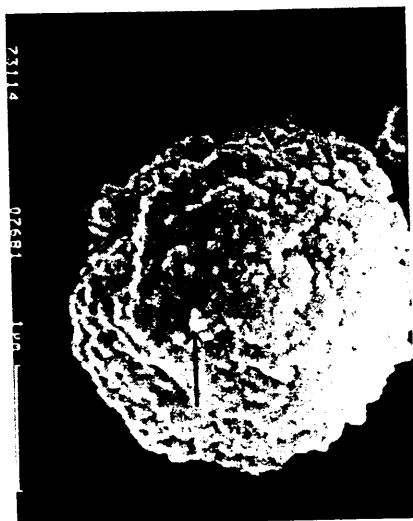


Figure 5. SEM-micrograph of a spray agglomerate in the BaO-Al₂O₃-SiO₂-system (arrow marks initial particle).

gel route in the preparation of crystalline materials such as YBa₂Cu₃O_{7-x} superconductors is the generation of thin films. Dip coating and subsequent thermal treatment of the YBa₂Cu₃O_{7-x} gel layers lead to homogeneous superconducting films. The media-temperatures of the transition temperature T_c which depends on the substrate [4] and the preparation conditions (O₂-partial pressure, temperature) requires further investigations. Preliminary measurements on pressed pellets indicated a sharp onset at a temperature of 95 K.

CONCLUSION

The sol-gel process by means of complexation is a successful method of synthesizing high melting glasses such as barium-alumina-silica glasses and generating homogeneous high-T_c YBa₂Cu₃O_{7-x} films.

ACKNOWLEDGEMENT

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METAL OXIDE FILMS FROM CARBOXYLATE PRECURSORS

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ABSTRACT

ZrO₂ and Ba₂YCu₃O_{7-x} metal oxide films were prepared from carboxylate precursors. The zirconia films were prepared from Zr octoate and the Ba-Y-Cu-O compound synthesized from a mixture of the metal neodecanoates. Dense, adherent ZrO₂ films were obtained on Si. Dense, superconducting Ba-Y-Cu-O films were also fabricated utilizing the octoate-derived ZrO₂ as a bonding surface and diffusion buffer.

Introduction

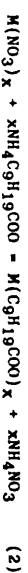
Metal oxide films derived from liquid precursors have emerged as a viable alternative to physical and chemical vapor deposition techniques[1]. The latter methods can involve significant expense and must be adjusted for complex compounds, such as the high temperature superconductors and doped tungsten bronze structures [2]. Liquid precursor methods offer the advantage of atomic scale mixing of the chemical species and close control of deposition process.

Preparation methods for the chemically derived ceramic films include sol-gel techniques, metal salts, and the use of carboxylate precursors. The metal-alkoxide precursors, typically in an organic solvent, are spin deposited onto a suitable substrate. Hydrolysis and condensation (polymerization) of the metal-alkoxide film occurs after deposition, and is controlled by solvent composition. Subsequent heat treatment, at temperatures markedly below those needed for normal ceramic solid state densification, drives off residual solvent and breaks down the polymerized "gel". The film then typically undergoes a viscous sintering process [3]. Liquid-phase deposition techniques utilizing citrate and nitrate liquid precursors have also been reported [4]. These avoid the hydrolysis and condensation steps characteristic of the sol-gel process, and many of the accompanying environmental requirements (controlled ambient, drying, etc.). As these compounds are carried in an aqueous solution, densification of the film involves only the evolution of the water and nitrate components preliminary to sintering of the oxide film components.

The investigation of metal carboxylates as potential paint driers [5], and the development of the BaTiO₃-type materials from metal nitrates, ammonium hydroxide and neodecanoic acid by Vest [6], introduced another method of deposition of metal oxide films from liquid precursors. Here the metal nitrate is dissolved in water and combined with ammonium neodecanoate from the reaction:



The metal neodecanoate is formed by further reaction with the metal nitrate:



Xylene or another nonpolar organic solvent is used to extract and separate the metal neodecanoate (which is insoluble in water). The solvent is subsequently removed by standard techniques yielding the metal neodecanoate compound, which is air stable.