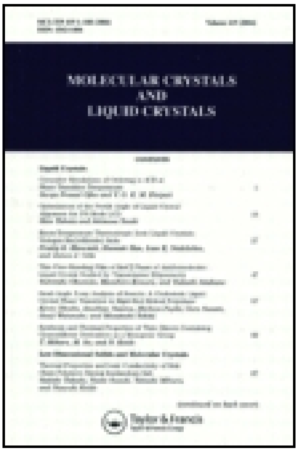

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Preparation and Properties of Superconducting Bi-Pb-Sr-Ca-Cu-O Shaped Materials by the Alkoxide Process

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PREPARATION AND PROPERTIES OF SUPERCONDUCTING Bi-Pb-Sr-Ca-Cu-O SHAPED MATERIALS BY THE ALKOXIDE PROCESS

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Abstract Bulk, thick film and fiber were prepared respectively by the sol-gel route using the same solution. The advantages of the sol-gel method are discussed with the superconducting properties.

INTRODUCTION

The sol-gel method using metal alkoxides has been said to be a promising way for synthesis of ceramics. Because the process would be better than other methods for the preparation of viscous and highly homogeneous solutions. Its advantages actually have been found in applying to optical glasses.[1] Generally the sol-gel route is thought to be characterized by low temperature synthesis of glasses and glass-ceramics. Recently many research workers have reported superconducting films,[2] fine powders[3] and fibers[4] by using the sol-gel and its similar methods. No one, however, has found the decisive merit of this way in the field of fabricating high-Tc superconductors. One of the aims of this study was focused on finding the true advantages of the sol-gel method in the fabrication of high-Tc superconducting oxides.

EXPERIMENTAL

Figure 1 shows the process for the direct formation of superconducting bulks, films and fibers. Bi,Pb,Sr,Ca and Cu ethoxides were used as starting materials. These ethoxides were mixed in a dry box and then dissolved by heating in an aqueous solution of diethylenetriamine(DETA) and acetic acid. The stoichiometry of the homogeneous solution with respect to Bi:Pb:Sr :Ca:Cu was 0.96 :0.24:1.00:1.15:1.60. Coating film (Film A) was prepared by dipping MgO substrates into the initial homogeneous solution. A viscous solution was produced by heating the initial solution to 90 ℃. The viscosity of the solution increased during heating, which was controlled by the heating time. The viscous gel solution was diluted with benzen. Coating film (Film B) was prepared using this diluted solution. Fibers were drawn manually from the viscous gel solution by using a glass rod. Subsequently the viscous solution became a rigid bulk gel after continuous heating. The two kinds of coated films, drawn fiber and stood bulk gel were preheated very carefully at 250 ℃ for 1 hr. After that, these were fired at 850 ℃ for 8 hr in air. The properties of the viscous gel and the fired ceramics were investigated.

RESULTS AND DISCUSSION

The viscosity of the solution increased with heating time as shown

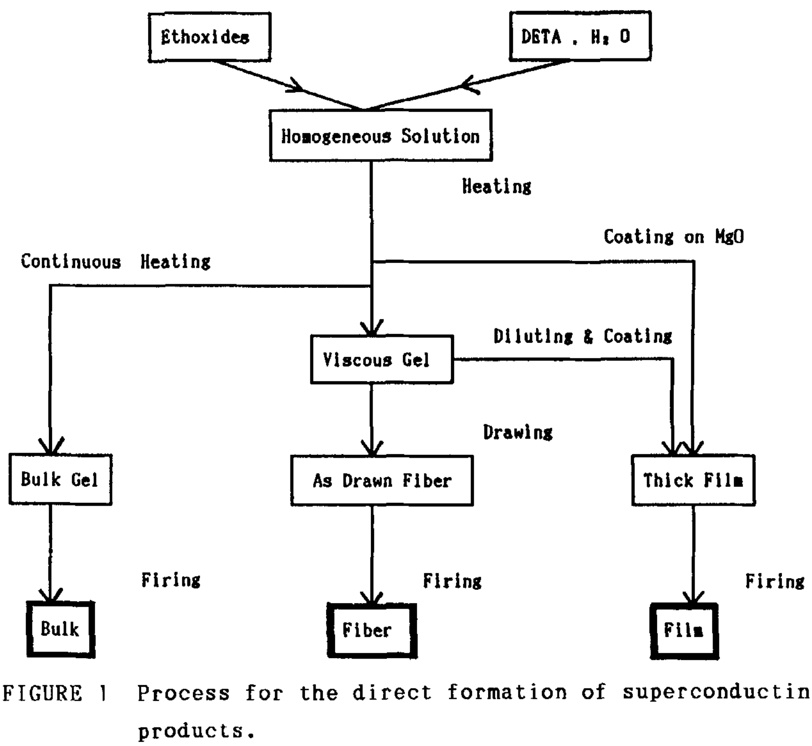

FIGURE 1 Process for the direct formation of superconducting products.

in Figure 2. Each viscosity value which was used to prepare the shaped products is indicated in the figure. After heating for around 350 min, the viscosity of the solution increased rapidly and then rigid gel was formed. It was found that the viscous solution (gel) showed spinnability in the viscosity range of 50-2000 poise. Long fiber (approximately 150 cm) was obtained by continuous drawing in the viscosity of 500 poise. The network among some intermediate products containing DETA would be formed in the viscous gel. DETA is thought to act as complexing and chain growth agents. In the TGA and DTA curves of the viscous gel, rapid weight loss took place from 180 to 260 ℃. Then the weight slowly decreased up to 600 ℃. These changes are considered to be due to volatile loss of remaining DETA in the gel and the thermal decomposition of the gel. In the temperature range of 180-320 ℃, decomposition of the remaining ethoxy groups and the simultaneous condensation dehydration of OH groups would occure in the gel. The melting poit of the ceramics was thought to be 875 ℃. It was confirmed by the X-ray diffraction analysis that all the fired

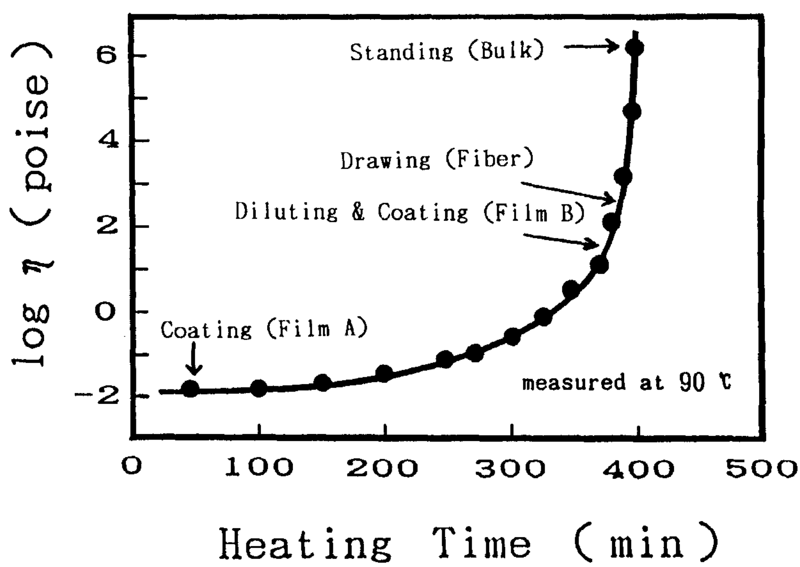

FIGURE 2 Logarithm of viscosity for the gel solution versus heating time.

products contained a high Tc (110K) phase. From the X-ray diffraction patterns, the fired thick film was shown to have the preferable c-axis orientation.

Figure 3 shows SEM micrographs of the surfaces for the fired products. The fired bulk was porous and had a hollow structure. This is supposed to be caused by the difficult decomposition of carbonaceous residue contained in the highly polymerized gel. Accordingly, the rigid bulk ceramics can not be obtained from the stood bulk gel through this alkoxide process. The fired film(Film B) has comparatively smooth surface, though it has many particle-shaped deposits. The fired film (Film A) from the solution also showed the similar image to this photograph. The fired fiber seems to be porous as shown in Figure 3 (c). However that has not so higher porosity as the Y-system fiber[5,6] prepared by the similar method has. The fiber was brittle and had a low strength. The diameter was 20-30 μm, which was slender than that of Y-system fiber.[5,6]

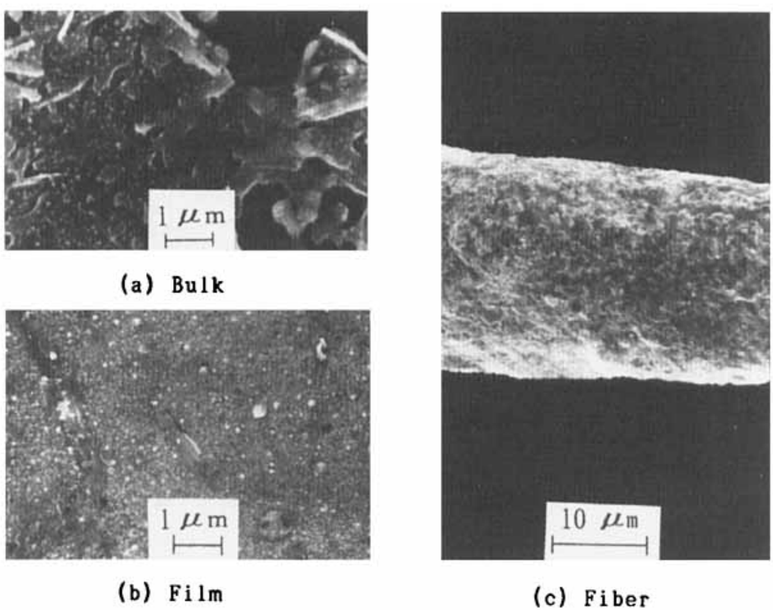

FIGURE 3 SEM micrographs of the surface for the fired products.

TABLE 1 Values of Tc and Jc for the fired products.

	Bulk	Fiber	Film A	Film B
Tc (K)	75	83	82	90
Jc(A/cm²) at 77K , 0 T	−	95	110	230

Table 1 shows the results of Tc (zero resistance temperature) and Jc (critical current density at 77 K, 0 T) for these fired products. The fired bulk has a lower Tc than those of the others . The interesting point is that Film B has a higher Tc than that of Film A. Film B from the viscous gel has higher Tc and Jc values than those of Film A. Therefore, it is generally recognized that the ceramics showing better superconducting property should be obtaind by using the viscous gels having the network structure for Bi-system oxides.

CONCLUSIONS

It should be important that the viscous gels having strong networks among oxides would be used for fabricating better superconducting ceramics. The positive use of the viscous gel having a ease of processability will bring arbitrary-shape superconductors, such as fibers. More work is thought to be requred to optimize the process that the superconducting products can be fabricated successfully using the advantages of the sol-gel method.

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