

## 열분해법에 의한 고온 초전도 합성

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## Fabrication of High Tc Superconductor Using Thermal Pyrolysis

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A high Tc superconducting with a nominal composition of  $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_y$  was prepared by the citrate method. The solid precursor produced by the dehydration of the gel at  $120^\circ\text{C}$  for 12h is not in the amorphous state as expected but in a crystalline state. X-ray diffraction peaks of nearly the same angular position as the peaks of high Tc phase were observed in the precursor. After pyrolysis at  $400^\circ\text{C}$  and calcination at  $840^\circ\text{C}$  for 4h, the (001)peak of the high Tc phase was clearly observed. Experimental results suggest that the intermediate phase formed before the formation of the superconducting phase may be the most important factor in determining whether it is easy to form the high Tc phase or not, because the nucleation barriers of the two superconducting phase may be altered by the variation of the crystal structures of those intermediate phase.

**Key Words** : BSCCO, superconductor

### 1. 서론

The discovery of superconductivity in the  $\text{BiSrCaCuO}$  with two superconducting temperatures. Compared with the earlier developed  $\text{YBaCuO}$  superconductor, this oxide system contains no rare earth element and has greater chemical resistance against moisture, but the critical current density,  $J_c$ , is lower and requires prolonged annealing to form the high Tc and other phase. So far, much effort has been devoted to the fabrication and application of this superconducting oxide system. Generally the preparation of superconducting oxides by conventional solid state reaction relies upon the repeated milling and sintering of an oxide and/or carbonate mixture. With such a process, the time required to obtain acceptable homogeneity is very expensive and serious contaminations may be introduced during the milling process. On the other hand, chemical solution methods are much more efficient in the production of mixtures of high homogeneity. Among these solution methods, the amorphous citrate process makes it relatively easy to form the desired oxide compound at a lower temperature or during a shorter reaction time, because the amorphous citrate process relies upon the solid amorphous precursor material prepared by

the dehydration of gels, which is produced by the addition of citric acid into a solution containing metal salts such as nitrates. The amorphous solid may have a high degree of homogeneity and a more open structure through which atoms can easily diffuse without having to overcome the high activation barrier. In this paper, we reported the production of the  $\text{BiSrCaCuO}$  high Tc superconductor by the citrate method.

### 2. 실험

The Bi high Tc superconductor with nominal composition of  $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_y$  was prepared by the citrate method. A mixture of nitrate salts in a suitable molar ratio with total weight 50gm was dissolved in 150ml distilled water. The nitrate solution was then vigorously stirred with a few drops of 60wt%  $\text{HNO}_3$  solution added to assist the dissolution. After a clear solution was obtained, powered citric acid and ethylene glycol were added. The resulting solution was colored light blue and was magnetically stirred and heated between  $70$  and  $90^\circ\text{C}$ . A vigorous reaction occurred and enormous amount of NO gas evolved during this procedure. When a vigorous liquid began to set into a gel. Subsequently, the gel was dehydrated at  $120^\circ\text{C}$  for 12h, while the color of

the gel changed from blue to green, and finally a solid precursor material of a brownish yellow color was obtained.

### 3. 결과 및 고찰

Figure 1 shows the XRD patterns where curve (a) shows the XRD pattern of compacted precursor material produced by the hydration of the gel at 120°C for 12h show the XRD pattern of the green compacts of the powder after calcination at 400°C, 600°C, and 840°C, respectively. Fig.1 shows that the structure of the precursor is not in the amorphous state but in the crystalline state. Some minor peaks in Fig.1 shows were slight varied in different samples of the same batch, were identified as the traces of various oxides, hydroxides and residual nitrate salts. The other major peaks, which always existed without significant change to the ratio of the intensities, and could not be search matched with the JCPDS card inorganic phases data cards, may belong to the citrate salts or compounds decomposed from the citrate salts. Among these major peaks, some marked by dots in curve could be indexed in an angular sequence as (004), (103), (008), (016), (0010), (0012), (0016) and (0020) peaks of the high T<sub>c</sub> phase. By comparing the spacings calculated from the angular positions of the 8 peaks in Fig.1 stated above with those of the high T<sub>c</sub> phase based on the tetragonal unit cell with a=b=5.396Å and c=37.180Å, the mismatches can all be seen to be less than 0.4%. Since the intensity of the (004)peak of the real high T<sub>c</sub> phase is very weak, while the peak in Fig.1 indexed as (004) of the high T<sub>c</sub> is the main peak of precursor, and also because the precursor is an insulating material, we can not say that the high T<sub>c</sub> phase was definitely formed at such a low temperature as 120°C.

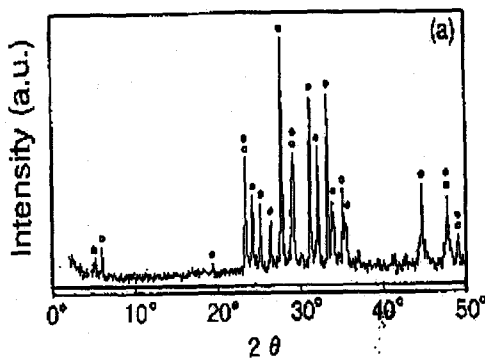


Fig. 1. XRD pattern of superconducting precursor.

Fig.2 shows the resistance vs temperature curves of the sintered pellets with their XRD pattern in Fig.1. Their zero resistance temperature, T<sub>c</sub> was 110K. The zero resistance temperature was found to increase

with the sintering time. Since no appreciable increase was observed in the relative amount of the high T<sub>c</sub> phase with respect to the low T<sub>c</sub> phase, and it is known that the current density is limited by intergranular contacts in polycrystalline superconducting oxides, the increase of the zero resistance temperature is mainly attributed to the increase of contact areas between grains during the sintering process.

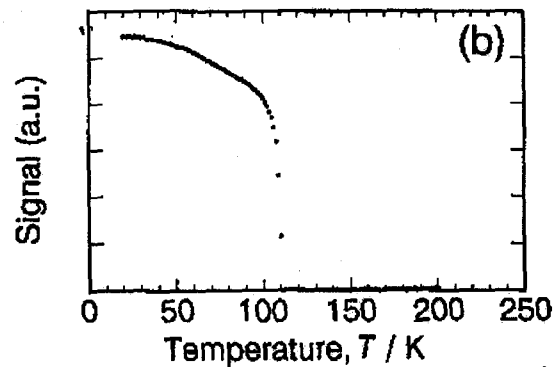


Fig. 2. The resistance vs temperature curves of the pellets sintered at 840°C for 10h.

### 4. 결론

Although the precursor material prepared in the citrate method was not in the amorphous state as expected, volume fraction of the high T<sub>c</sub> phase was obtain calcination at 840°C for a short time. Further the precursor may suggest ways of altering the procedures to increase the volume fraction of the high T<sub>c</sub> phase and the T<sub>c</sub> at lower reaction temperature with a shorter sintering time.

### 감사의 글

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### 참고 문헌

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