

Synthesis of BiSrCaCu(Ni)O Ceramics from the Gel Precursors and the Effect of Ni Substitution[†]

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Superconducting BiSrCaCu(Ni)O ceramics have been prepared by the gel method using an aqueous solution containing a tartaric acid. The aqueous solution of metal salts was concentrated without precipitation. The precursor so prepared was homogeneous and calcined at 825 °C for 24 h to produce superconducting phase. The thermal decomposition of gels, the formation of superconducting phase, and their ceramic microstructure were studied using IR, TGA, XRD, resistance measurements, and SEM. This method is highly reproducible and leads to powders with excellent homogeneity and small particle size for easy sinterability. The nickel dopant substituting for Cu gives rise to the gradual decrease of the T_c . Phase pure 2212 ceramics were obtained at 825 °C for 24 h. SEM pictures showed that liquid phase was formed when the samples were sintered temperatures higher than 825 °C.

Key Words : Superconducting ceramics, Gel precursor, Homogeneity, Calcination, Dopant

Introduction

Ceramic superconductors have been produced by a variety of techniques, the most popular of which have been the ceramic method and the chemical methods of coprecipitation and freeze drying. Each of these techniques has limitations and problems associated with the actual process and the quality of the material produced. Any synthetic scheme should start with inexpensive, readily available, and suitably pure reagents but should not require excessive time, labor, or specialized equipment. In addition superconducting products should possess several desirable qualities such as high phase purity, acceptable values of critical parameters, and small uniform particle size. Considerable efforts have been made in the synthesis, processing, and characterization of BiSrCaCu(Ni)O superconducting ceramics because these materials have a higher T_c and good chemical durability (resistance to moisture), and also they contain no rare earth elements.¹⁻³ The Bi-based superconductor system actually consists of three different superconducting phases with very similar crystal structures. The general chemical formula for these phases can be written as $\text{Bi}_2\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{4+2n}$, with $n = 1, 2, 3$ corresponding to the 22 K (2201 phase), 80 K (2212 phase; low T_c phase) and 110 K (2223 phase; high T_c phase) respectively.^{4,5} They have single, double, and triple layers of CuO₂ plane in a unit cell. Because of the similarity of their structures and thermodynamics of formation, all three phases can be present to some degree in the average sample.⁶⁻⁹ Only careful control of the processing conditions for these samples would permit formation of one of these phases in pure form.

In order to attain higher homogeneity, smaller particle size

and better controlled stoichiometry in the BiSrCaCuO system, several methods have been employed by various workers: solid state reaction,^{10,11} oxidation of liquid quenched precursor alloys,¹² matrix reaction,¹³ crystal growth,¹⁴ and coprecipitation method.^{15,16} However, unlike the YBaCuO systems, in which powders and films have been fabricated by several solution techniques, few studies have used solution technique to obtain Bi-base materials and most of these techniques are for films.^{17,18} The reason may be that, despite the good homogeneity usually obtained through this process, the chemistry involved in a quaternary system is quite complex and the possibility of finding compounds with common properties and solvents for each of the constituent elements is much lower.¹⁹⁻²² In general, the sol-gel method using organometallic compound has advantage in the preparation of homogeneous ceramic materials because the precursors consist of small particles that exhibit a very high chemical activity and they are sintered easily into the oxide at relatively low firing temperatures. One of the several different alternate approaches is the gel procedure using specific gelling reagent. The approach is as follows: First prepare the gel from a homogeneous solution, which can then be decomposed to the oxides under mild thermal conditions. These oxides react to form the ceramic.

This paper will describe the preparation of the 80 K phase $\text{Bi}_2\text{Sr}_2\text{Ca}(\text{Cu}_{1-y}\text{Ni}_y)_2\text{O}_x$; low T_c phase, by the gel method using a tartaric acid. Also, the gelation of the starting solutions, the processes of decomposition of the precursors and the crystallization of various phases, and the studies on the Ni substitution for Cu will be discussed through the paper. The doping of nickel into Cu will change the transition temperature with concentration of nickel.

Experimental Section

Superconducting oxides of the $\text{Bi}_2\text{Sr}_2\text{Ca}(\text{Cu}_{1-y}\text{Ni}_y)_2\text{O}_x$ (2212

[†] Author cordially dedicates this paper to Professor Sang-Chul Shim who had pioneered the photochemistry research in Korea.

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phase), where $x = 0$ and 0.1 , were prepared from the high purity grade $\text{Bi}(\text{CH}_3\text{COO})_3$, $\text{Sr}(\text{CH}_3\text{COO})_2 \cdot 1/2\text{H}_2\text{O}$, $\text{Ca}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$, $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot 1.08\text{H}_2\text{O}$, Ni (fine metal powder), which were purchased from AESAR, Fisher Scientific, and Aldrich Chemicals. Experimental details of the preparation of a 10% nickel doped BiSrCaCuO sample are as follows: $\text{Bi}(\text{CH}_3\text{COO})_3$ (0.03 mol, 11.583 g) was dissolved in 500ml acetic acid solution of the composition, $\text{H}_2\text{O} : \text{CH}_3\text{COOH} = 6 : 1$ by volume, and stirred for 12 hours at room temperature (Bismuth acetate dissolves only in the acid solution). Nitric acid in which Ni powder was dissolved was added to the Bi solution. $\text{Sr}(\text{CH}_3\text{COO})_2 \cdot 1/2\text{H}_2\text{O}$ (0.03 mol, 6.441 g), $\text{Ca}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ (0.015 mol, 2.643 g), $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot 1.08\text{H}_2\text{O}$ (0.027 mol, 5.429 g) were dissolved in the Bi solution so that the molar ratio of the cations became Bi : Sr : Ca : Cu : Ni = 2 : 2 : 1 : 1.8 : 0.2 for 10% Ni substitution for the Cu. Metal acetates are analysed to determine their levels of hydrated water before use. They are converted to the corresponding oxides at sufficiently high temperatures (800-900 °C). The amount of water has been determined according to their stoichiometric reaction (Gravimetric analysis).

Either NH_4OH or $\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2$ was added dropwise into the solution with constant stirring until the pH reached 4.8 (as determined by a precipitation test). When pH exceeded 4.8, a white precipitate (bismuth nitrate) was observed. The addition of base raises pH of the solution and this high pH helps the formation of the gel. After adding tartaric acid (0.5 times the mole ratio of Cu), the solution was stirred for another 12 hours and kept in an uncovered oversized petri-dish. Water was evaporated at 80 °C to become viscous gel finally leading to a dried dark blue gel. The precursor was pulverized and preheated at 200 °C to evolve NO_2 and acetic acid. This preheat avoids phase separation by explosive reaction. The temperature was slowly raised to 600 °C and maintained for 8 hours to ensure the decomposition of the organic precursors such as the carbonates and acetates used. The sample was finally sintered between 815 and 830 °C for 24h, then cooled down in the furnace. These conditions were chosen because after a sinter at the temperatures higher than 830 °C, the partial melting of the powdered sample was observed. The temperature of the furnace was monitored using the thermocouple which was connected to the recorder to follow the temperature. Thermogravimetric analysis (TGA) and infrared spectra (IR) were used to study the thermal decomposition of the precursors and its phase transformation. The dc electrical resistance of the bar-shaped sintered sample was measured by four-probe method using a Keithly model 181 nanovoltmeter. The precursors, intermediates, final products were characterized by X-ray powder diffraction (XRD) using $\text{CuK}\alpha$ radiation at 45 kV, 30 mA. The data was compared by the Rigaku computer system with a CD-ROM powder diffraction file.

Results and Discussion

Transparent, amorphous gel in the BiSrCaCu(Ni)O system was formed by concentrating the aqueous solution of metal

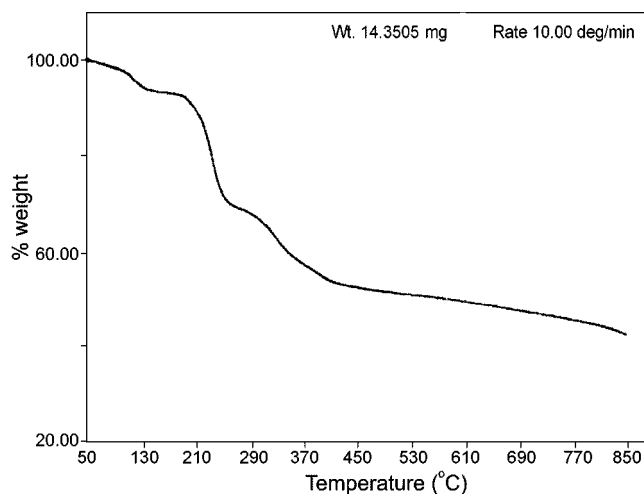


Figure 1. TGA thermodiagram of the BiSrCaCu(Ni)O precursor while ramping at 10 °C/min.

acetates containing acetic acid, nitric acid, and tartaric acid. Tartaric acid was found to be effective in gel formation, especially in preventing the crystallization of copper acetate hydrate during the concentration.^{13,14} Figure 1 is a TGA of a precursor prepared through the gel method. The picture indicates that the material has undergone a weight loss even below 180 °C due to the loss of waters which are chemically bound to the hydrates; *i.e.*, $\text{Sr}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$, $\text{Ca}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$, $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$. Major decomposition occurs between 180 °C and 500 °C (about 50% of the original weight loss). After 500 °C, little change occurs at higher temperatures. Most decomposition is complete below temperature.

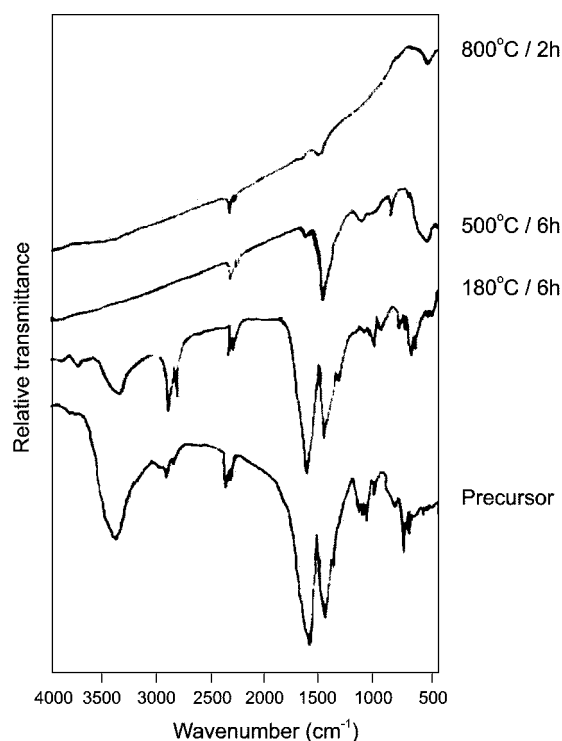


Figure 2. IR spectra of the precursor and its calcination products.

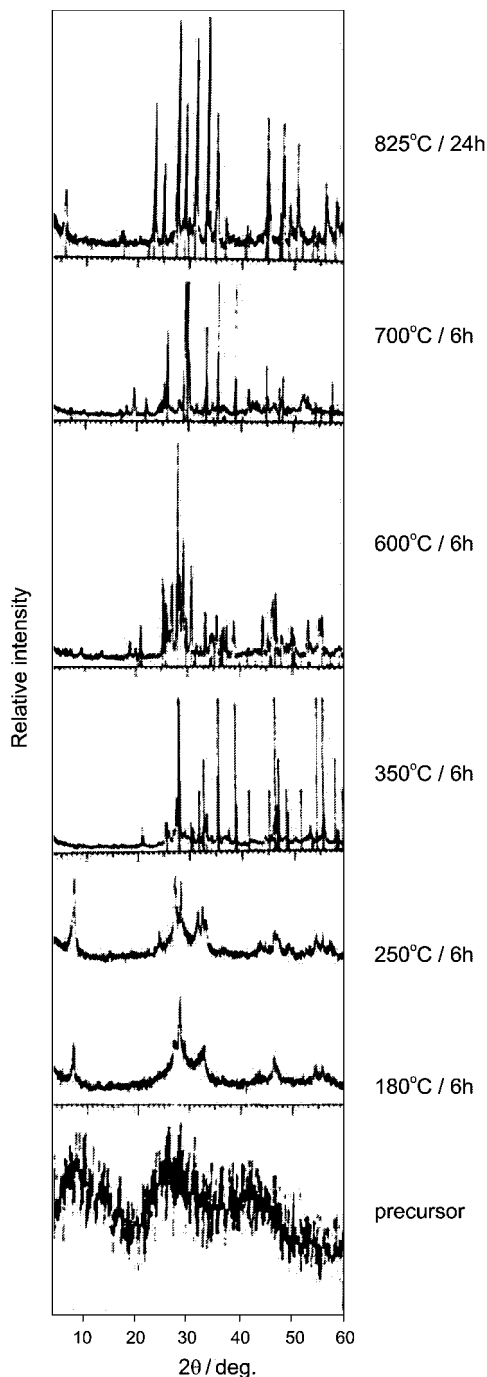
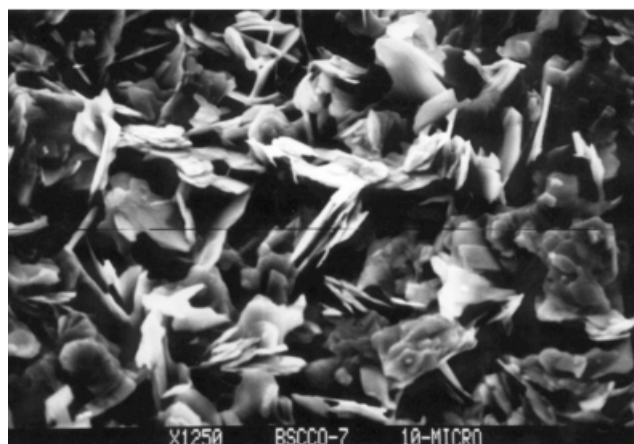
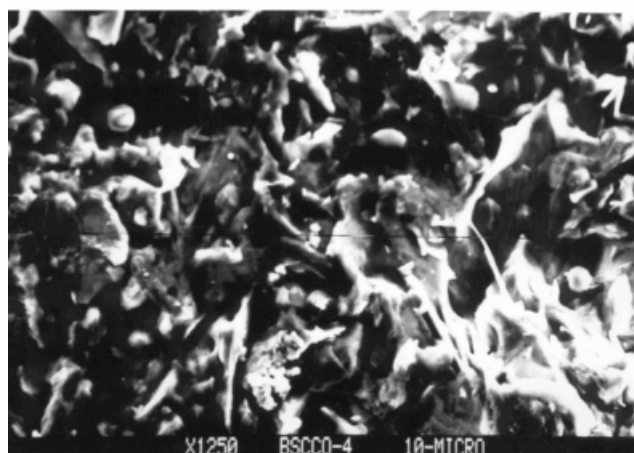


Figure 3. X-ray diffraction patterns of the as prepared precursor system after heating at different temperatures.

Gradual weight loss of the precursor indicates a stepwise decomposition of the precursor by 500 °C. Abrupt changes were not observed during the process. IR spectra show the conversion of the precursor to the final product (Figure 2). The presence of carboxylic groups and water are confirmed by their strong absorptions around 3400 cm^{-1} . Water and acids substantially disappear when the precursor was heated at 180 °C for 6h. Metal carboxylates ($\text{C}=\text{O}$ at 1560 cm^{-1} , $\text{C}-\text{O}$ asymmetric stretching at 1410 cm^{-1}) and nitrates ($\text{N}-\text{O}$ at 1400 cm^{-1}) were converted to carbonates ($\text{C}-\text{O}$ for CO_3^{-1} at 1450 and 870 cm^{-1}) after calcination at 500 °C for 6 h. In the



(a)



(b)

Figure 4. Scanning Electron Micrographs of BiSrCaCu(Ni)O samples: (a) 825 °C for 24 h (b) 845 °C for 24 h.

spectrum, the $\nu(\text{C}=\text{O})$ vibrations at 1560 cm^{-1} of $\nu_{\text{as}}(\text{COO}^-)$ and 1410 cm^{-1} of $\nu_{\text{s}}(\text{COO}^-)$ indicates that COO^- groups are coordinated to a metal ion. These peaks including $\text{N}-\text{O}$ peak at 1400 cm^{-1} were converted to carbonates ($\text{C}-\text{O}$ for CO_3^{-1} at 1450 and 870 cm^{-1}) after calcination at 500 °C for 6 h. On heating to 800 °C for 2 h, most carbonate peaks have disappeared. X-ray powder diffraction analysis was used to follow the phase development as well as its phase identification. The precursor powder is amorphous at room temperature as shown in Figure 3. In the sample preheated at 180 °C and 250 °C, bismuth oxide Bi_2O_3 and nickel nitrate $\text{Ni}(\text{NO}_3)_2$ are found. At 350 °C, Bi_2SrO_y , CaCO_3 , and CuO are also found. $\text{Bi}_2\text{Sr}_2\text{CuO}_y$ (2201 phase) appears at 600 °C through the reaction of Bi_2SrO_y and CuO . At 700 °C, $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_x$ (2212 phase) appears and at this point phases corresponding to CaO , CuO , and carbonates of Bi and Sr are also identified. XRD pattern of the final product obtained at 825 °C for 24 h shows good match with standard 2212 pattern as seen in the Figure 3.

Figure 4 shows SEM photographs of the sample described above. The microstructure of the sample was greatly affected by the calcination temperature. SEM picture obtained from the sample sintered at 825 °C (Figure 4a) shows the thin

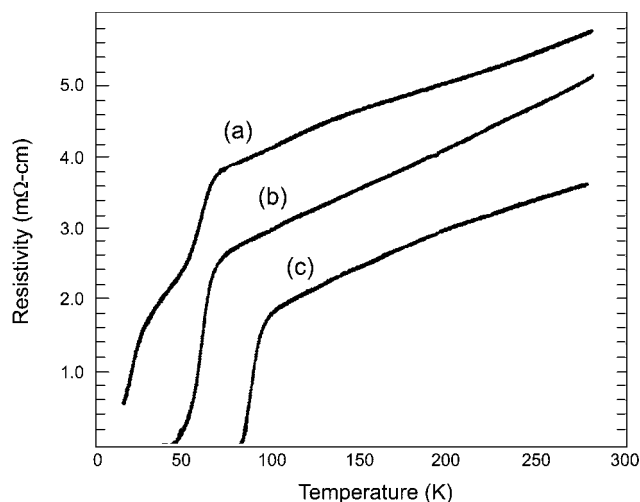


Figure 5. Temperature dependence of electrical resistance for (a) $\text{Bi}_2\text{Sr}_2\text{CaCu}_{1.8}\text{Ni}_{0.2}\text{O}_x$ after 800 °C for 24 h (b) $\text{Bi}_2\text{Sr}_2\text{CaCu}_{1.8}\text{Ni}_{0.2}\text{O}_x$ after 825 °C for 24 h (c) $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_x$ after 820 °C for 24 h.

plate-like phase characteristic of bismuth containing superconductor. Sintering at higher temperatures resulted in a change. Figure 4(b) is the picture taken from the sample sintered at 845 °C for 24 h. Evidence of liquid phase formation, even though no second phases are detectable by X-ray diffraction, can be now noted as indicated by the smooth, spherical pores. It means the increase of liquid phase formation as temperature increases. The BiSrCaCuO ceramics contain two main superconducting phases. It is known the incorporation of Pb ions for Bi of the system causes a higher volume fraction of the phase. This suggests that the addition of foreign elements to the BiSrCaCuO system could change the free energy of formation of the high and low T_c phases. The resistance curves of the 10% Ni doped 2212 sample sintered at 800 and 825 °C for 24 h respectively are shown in the Figure 5(a) and 5(b). Figure 5(a) shows a two step transition, indicating that the sample consists of the mixture of 2201 and 2212 phases, which was expected in the XRD patterns. It suggests that the complete transformation from the 2201 phase to the 2212 phase is achieved by heating up to 825 °C. Figure 5(c) is the curve obtained from $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_x$ sample. It shows T_c (zero) at 78 °C. The structure of $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ is orthorhombic and is built up of calcium and metal-oxygen layers with a stacking sequence Ca-CuO₂-SrO-BiO-SrO-CuO₂-Ca in the c-direction. The pairing of the carriers in the CuO₂ planes is responsible for the superconductivity in $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$. A replacement of some of the copper atoms will change the superconducting properties and alter the electronic structure. $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ has only one equivalent Cu site. Close similarities of the two cations with respect to their ionic size, their valency and fluctuating valence are expected to make the substitutional effects relatively less ambiguous. The substitution gave rise to the gradual decrease of the T_c . The cationic dopants substituting for Cu tend to inflict disorder in Cu-O networks which at a higher dopant level may show semiconducting-like resistance behavior. However, the effect

of Ni substitution on T_c is not so large. There are two main keys to understand the effect of foreign element replacement in CuO plane: (1) The changes of the carrier concentration and microstructure induced by the replacement. (2) Magnetic scattering of carriers caused by magnetic ions substitution. The effect on T_c is not so large compared to Zn. Although with respect to their ionic size both Zn and Ni match closely with Cu, the valence of Zn is fixed while that of Ni can fluctuate. Because of its rather rigid divalency, Zn in CuO networks serves as an obstacle which impedes metallic behaviour and superconductivity. Here the decrease of T_c should be mainly attribute to the magnetic scattering induced by Ni ions ($\text{Ni}^{+2}/\text{Ni}^{+3}$) in CuO plane.

Conclusions

Superconducting $\text{Bi}_2\text{Sr}_2\text{Ca}(\text{Cu}_{1-y}\text{Ni}_y)_2\text{O}_x$, where $y = 0$ and 0.1, were prepared through the gel method using an aqueous solution of organic metal salts containing acetic acid and tartaric acid. It was found that COO^- groups were coordinated to a metal ion and converted to carbonates after calcination at 500 °C. 2212 phase appeared at 700 °C and phase pure 2212 powders were obtained at 825 °C for 24 h. SEM pictures showed that liquid phase was formed when the samples were sintered at 835, 845, and 855 °C, for 24 h respectively. It showed the increase of liquid phase formation as temperature increased. $\text{Bi}_2\text{Sr}_2\text{CaCu}_{1.8}\text{Ni}_{0.2}\text{O}_x$ sample sintered at 800 °C for 24 h showed a two step transition indicating that it consisted of the mixture of 2201 and 2212 phases. T_c (zero) of $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_x$ and $\text{Bi}_2\text{Sr}_2\text{CaCu}_{1.8}\text{Ni}_{0.2}\text{O}_x$ samples sintered at 825 °C for 24 h were 78 K and 47 K respectively. The substitution gives rise to the gradual decrease of the T_c . The cationic dopants substituting for Cu tend to inflict disorder in Cu-O networks which at a higher dopant level may show semiconducting-like resistance behavior. However, the effect of Ni substitution on T_c is not so large. It can be attributed to its resemblance to Cu. Ni has not only close ionic size to Cu, but its valence can fluctuate.

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