窒酸鹽과 水酸化나트륨을 써서 졸-겔 法으로 만든 $YBa_2Cu_3O_{7-x}$의 特性分析

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CHARACTERIZATION OF $YBa_2Cu_3O_{7-x}$ MADE BY A SOL-GEL PROCESS USING NITRATE SALTS AND SODIUM HYDROXIDE

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ABSTRACT: A sol-gel processing of $YBa_2Cu_3O_{7-x}$ superconductor using metal nitrate salts and sodium hydroxide as the starting materials has been investigated because of the need to produce pure, hompgeneous superconducting materials.

Since the precipitation of barium hydroxides can be obtained only at high basiciti-es, the process has to be carried out Ca. pH 13 to get the simultaneous coprecipitation with the other metal hydroxides. The involved reaction mechanisms were investigated and intermediate and final products were characterized by means of thermogravimetric analysis (TGA), infra-red(IR) spectroscopy, X-ray diffraction(XRD) analysis, scanning electron microscopy(SEM), thermal mechanical analysis(TMA) and electrical measurement.

1. INTRODUCTION

Since the discovery of $YBa_2Cu_3O_{7-x}$ superconductor, the sol-gel processing has been tried to produce pure, homogeneous superconducting materials with various shapes such as bulks[3, 11, 13], fibers[9, 10] and coating films[4, 5, 6, 11, 12]. By starting with well mixed solution or sols, it is expected that homogeneity even on the molecular scale can be obtained. The term sol-gel processing usually refers to the fabrication of inorganic oxides (ceramics and glasses) using either metal alkoxide precursors or colloidal dispersions (sols) of hydrous oxides[1]. The term, sol, generally refers to a mixture of solid colloidal particles in a liquid. By removal of water from the sol, colloidal suspensions are gelled to yield a semirigid mass termed as a gel. Thus, the use of the term sol-gel can better be understand as an abbreviation of "solution-gelation." The cathegorization of sol-gel processing of $YBa_2Cu_3O_{7-x}$ superconductor includes the use of organometallics such as metal alkoxides[9, 10, 11, 12] and colloidal sols of the mixed metal hydroxides[2, 4, 12] as the precursors. However, the preparation of homogeneous $YBa_2Cu_3O_{7-x}$ material using the metal alkoxide precursors is difficult so that the copper alkoxides are very sparingly soluble

in organic solvents and the yittrium alkoxides are readly hydrolyzed by very small amount of water[6]. Accordingly, this paper only considers the applicability of colloidal sol processing to prepare $YBa_2Cu_3O_{7-x}$ material using metal nitrate salts and sodium hydroxide as the starting matterials. In this proposed procedure, the convensional metal carbonates being used as the agents to precipitate barium ions[3, 4] do not require for the precipitation of those ions, but sodium hydroxide is used only for the purpose of the precipitation

Homogeneous colloidal sols are formed, in situ, by the process of oxidation reaction of the mixed metal ions with sodium hydroxide.

However, metal halids, perchlorates can also be utilized to furnish the metal cations of yittrium, barium and copper, and pottasium hydroxide (inorganic alkaline)[3] and tetramethylammonium hydroxide (organic alkaline)[2, 4] can also be utilized to furnish the anions of hydroxide radicals.

The method of sol-gel process to prepare superconductors can offer several advantages in chemical, physical and technological aspects in resulting materials, for instance, the high grade of chemical purity due to exempting the process of comminution and grinding from the starting materials, the excellent homogeneity due to the mixing of the molecular level, the high sinterability due to the ultra-fine particles existing in the gel, and the high reproducibility can be realized if proper pH value and aging conditions are well controlled in the stage of the precursor phase of superconducting materials. Moreover, the sol-gel process is also possible to fabricate superconducting materials of various shapes such as plates, sheets, fibers and coating films.

In this paper, we present the experimental results concerning the preparation and the characterization of $YBa_2Cu_3O_{7-x}$ superconductor obtained by means of sol-gel process using metal nitrates salts and sodium hydroxide.

2. EXPERIMENTATL

2-1 ; material preparation

High purity nitrates, $Y(NO_3)_3 \cdot 5H_2O$, $Ba(NO_3)_2$ and $Cu(NO_3)_2 \cdot 3H_2O$ were weighed in molar ratio 1:2:3 and dissolved into warm distilled water to obtain an aqueous solution containing the mixed metal cations of yittrium, barium and copper. This solution was slowly poured into an aqueous solution of sodium hydroxide with vigorous motor stirring at the condition of solution basicities of pH 13 at room temperature.

The precipitates were isolated by filtration, washed with distilled water several times and dried overnight in drying oven at 120℃. Blue-white gel formed precipitates turned out to be black-tan. The black-tan precursors were thoroughly ground and calcined at 850℃ for 12 hours in air, followed by slow cooling. The calcined powders were pressed into pellet forms, and

these pellets were sintered at 900°C for 18 hours in the flow of oxygen and slowly cooled down to room temperature. The reaction scheme to obtain $YBa_2Cu_3O_{7-x}$ material is shown by the following.

$$(Y^{3+} + Ba^{2+} + Cu^{2+}) \xrightarrow{+OH^-} (Y, Ba, Cu)OH \xrightarrow[120°C]{-H_2O} (Y, Ba, Cu)O \xrightarrow[850°C]{\text{Calcination}} YBa_2Cu_3O_{7-x}$$

2-2 ; Thermogravimetric analysis(TGA)

TGA is usually used in order to get some understanding related to the decomposition mechanism occured and to determine whether to be yielded undesired compounds in the materals during pyrolysis process. TGA was observed under the condition of air atmosphere with the heating rate was 10°C/min.

Figure(1) shows the observed data concerning the information on the decomposition/oxidation occured in the gel precursor of $YBa_2Cu_3O_{7-x}$ material.

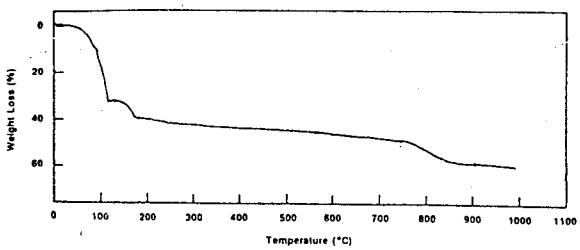


Fig.(1) TGA curve for the pyrolysis of the gel-powder

Three stages during the pyrolysis reaction can be seen on the data. The small weight loss between 130°C and 160°C appears to the dehydration of $Y(OH)_3$ and $Cu(OH)_2$. The gradual decrease in the temperature range 160°C - 750°C is assigned to the loss of oxygen from the material. The slight weight loss between 750°C and 900°C may be the decomposition of $Ba(OH)_2$ and some $BaCO_3$ formed by reaction between BaO and the ambient CO_2 gas.

2-3 ; Infra-red absorption measurement.

The calcined powders were investigated by infra-red spectroscopy in the energy range 400-3300cm^{-1}.

Figure (2) shows the characteristic infra-red absorption spectra of calcined powders at different temperatures.

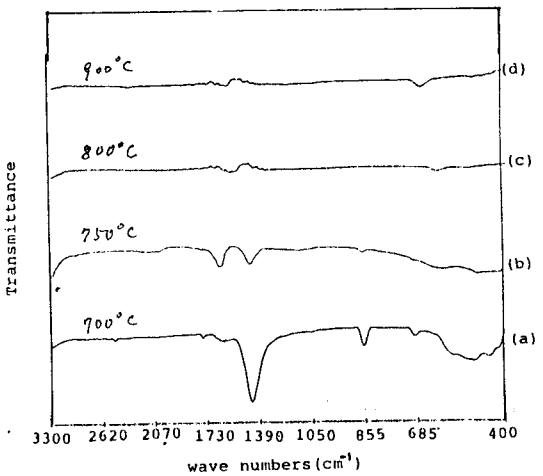


Fig.(2) IR absorption spectra of calcined powders at 700°c(a), 750°c(b), 800°c(c) and 900°c(d) in air for 12 hours

The strong absorption band appeared near 1450cm^{-1} of (a) spectrum shows a typical carbonate absorption band of the barium carbonate[16].

This carbonate phase also appears in the XRD pattern.

A weak absorption peak near 850cm^{-1} is due to the absorption of barium oxide[ ]. The IR spectrum of the calcined powder

at 750°C shows that the absorption peak of $BaCO_3$ is strongly diminished and the peak of BaO is almost disappeared. These facts suggest that the $YBa_2Cu_3O_{7-x}$ phase starts to be formed Ca. 750°C. Any other different peaks can't be detected in the (c) and (d) spectra, but small ripples still appear due to the traces of metal oxide impurities as well as the residual $BaCO_3$ not to be decomposed.

2-4 ; XRD analysis

The thermal treatment were investigated by X-ray diffraction analysis. Figure (3) shows the X-ray diffractograms and SEM imagines of calcined powders at different temperatures.

The strong $BaCO_3$ diffraction peak is detected on XRD pattern of (a), (b) and (c) spectra. For this reason, $Ba(OH)_2$ tends to form some $BaCO_3$ upon decomposition in ambient atmosphere due to the high reactivity between BaO yielded by decomposition and the ambient CO_2 gas.

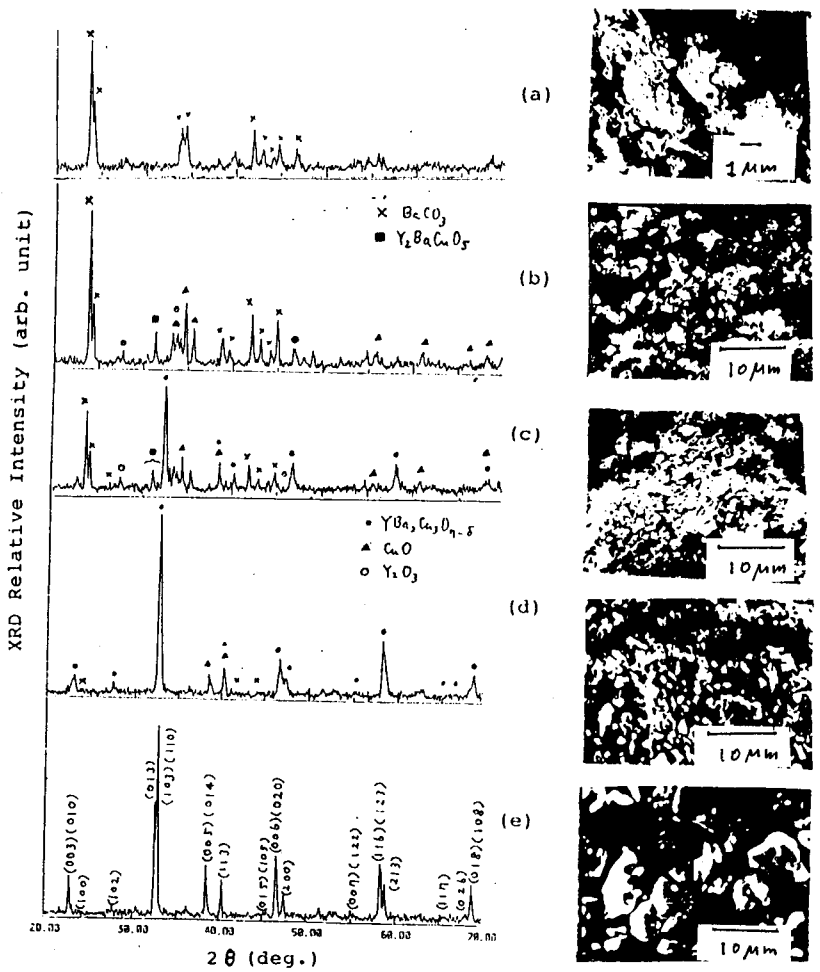


Fig.(3) XRD patterns and SEM images of calcined powders at room temperature(a), 700°c(b), 750°c(c), 800°c(d) in air for 12 hours and 900°c(e) in flow of oxygen for 18 hours

However, it is observed that, as increasing calcination temperature, the carbonate peaks are decreasing and $YBa_2Cu_3O_{7-x}$ phase shows gradual increasing.

Furthemore, X-ray diffraction patterns also reveal that the appreciable amounts of unreacted Y_2O_3, CuO as well as the trace of Y_2BaCuO_5 phase remained up to the calcination temperature, 800℃.

From those facts shown by the characteristics of IR and XRD, it is conclusive that the $YBa_2Cu_3O_{7-x}$ phase initiates the formation under the calcination condition, Ca. 750℃ for 12 hours and almost completes it under Ca. 800℃ for 12 hours, the conditions of which are obviously lower than those used for the conventional solid state method(900℃).

2-5 ; SEM analysis

The morphologies of calcined powders and sintered pellets were investigated using SEM. Figure (4) shows the morphology of the calcined powder at 800℃ in air for 12 hours. The powder can be seen to be 1-2㎛ in size. Figure (5) shows the mophology of calcined powder at 900℃ under the condition of oxygen flow. Although the explanation is not still conclusive how to the differences in morphology and grain size between two kinds of the respective powders being yielded, it is the obvious fact that the grain growth of the material is strongly dependent on the giving temperature and time. Figure (6) and Figure (7) show the SEM images of the fracture surface and the polished surface of sintered $YBa_2Cu_3O_{7-x}$ pellets.

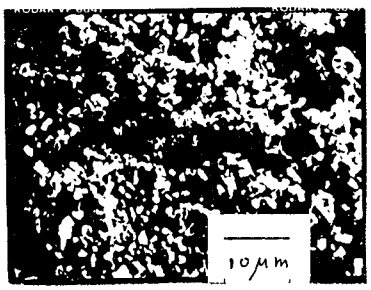


Fig.(4) Morphology of the calcined powder at 800°c in air

Fig.(6) SEM image of the fracture surface

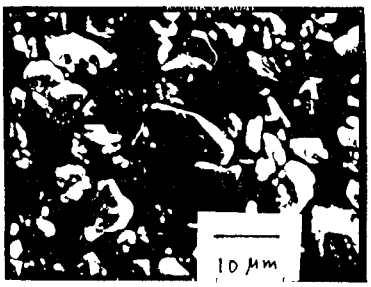


Fig.(5) Morphology of the calcined powder at 900°c in oxygen

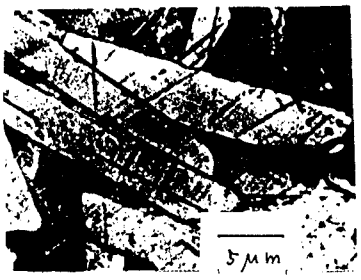
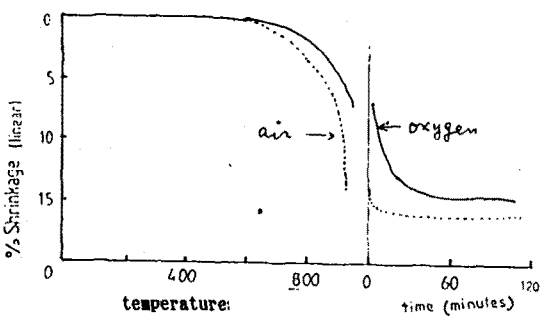


Fig.(7) SEM image of the polished surface

2-6 ; Thermal Mechanical Analysis (TMA)

TMA is observed using a dilatometer in order to obtain dilatometric data resulted during sintering[7]. A dilatometer usually indicates the amount of the expansion and contraction of samples as a function of temperature. The prepared gel-powder can be fabricated into pellet without the addition of any binder, and the pressing can be carried out through a single stroke of 1500 MNm^{-2}, in a cyclindrical die of the diameter, 3mm. And then the pellets are subjected to preoxidation under the condition of Ca. 600℃ and for 15 min. instead of the convensional calcination process. After then, the resulted black-tan colored pellets are subjected to sintering process in a dilatometer up to the temperature, 940℃, with the raising rate of 10℃/min. in the atmosphere of air as well as oxygen gas. Figure (8) clearly indicates that the densification is affected by temperature, time and atmospheric conditions.



Fig(8) The traces of sinterings

Flow of oxygen during cooling stage of sintered material is very important to obtain the better superconducting properties[7].

Figure (9) shows the other dilatometric characteristics on the sample subjected to sintering and subsequent cooling procedure in the oxygen atmosphere. A small bump observed at 680℃ in the cooling stage may be regarded as the indication of phase transition from tetragonal to orthorombic which means the lattice structure of the superconducting phase.

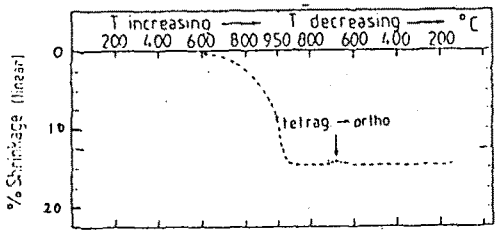


Fig.(9) Dilatometric curve showing the phase transition

2-7 ; Electical measurement

Standard four-probe technique is used to measure the dependence of electric resistivity of the sintered pellet. Figure (10) shows the obtained curve for the temperature dependence of resistivity.

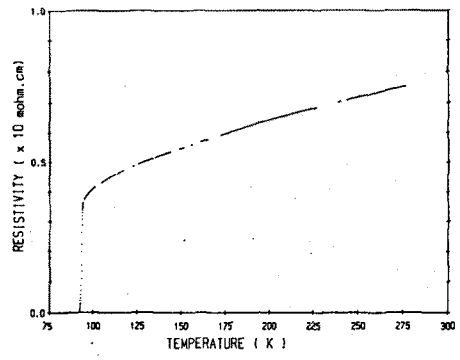


Fig.(10) The temperature dependence of electrical resistivity

Resistance starts to decrease abruptly at 94 K and drop to zero 92.8 K, hence the width of the superconduction transition is estimated to be 1.2 K. It is usually regarded that the width of the superconducting transition reflects the chemical inhomogeneities in the material, and much brother width means more impurities in it.

Accordingly the $YBa_2Cu_3O_{7-x}$ superconducting material prepared by proposed sol-gel method contains comparatively small amount of impurities, the fact of which is generally regarded to result the homogeneous morphology of the specimen.

3. Conclusion

(1) Superconducting meterial of $YBa_2Cu_3O_{7-x}$ phase can be produced in a homogeneous form by a sol-gel process using metal nitrate salts and sodium hydroxide at lower temperature than those used for the solid state method, but it is necessary a high grade control technique of chemistry to obtain the required homegeneity as well as ultra-fine structure of specimen.

We must realize the important factors such as the required stoichiometries, control of oxygen vacancies and anion defect control chemistry.

(2) SEM images confirms that the grain growth is related to the sintering temperature and time.

(3) The dilatometric data indicate that the densification kinetics is affected by tempreature, time and atmospheric conditions of the sintering.

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