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Synthesis of Functional Ceramics by the Mechanochemical - Sonochemical Concerted Reaction

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Mechanochemical and sonochemical synthetic methods for precursors of functional ceramics were examined respectively and simultaneously. Precursor gels of functional ceramics were mechanochemically treated by the agitation type milling using grinding media. Sonochemical reaction was caused by irradiation of ultrasonic converged wave to precursor gels at the frequency of hundreds KHz with input power of max.400W. Non-equilibrium reaction in solution of the vapor-liquid-solid coexisting condition in micron size regions by the mechanochemical and sonochemical concerted reaction enabled us to decrease the crystallization temperature of multi-elemental compounds such as oxide superconductors. Microscopic observation and spectroscopic analysis indicated the crystallization commenced from *in-situ* formed seeds of nanometer size in amorphous matrix of precursor was enhanced through following heating, which resulted in the lower crystallization temperature.

Key words: Sonochemistry, Mechanochemistry, Concerted reaction, Precursor, Crystallization

1. INTRODUCTION

Novel synthetic routes of functional ceramics have been developed with increasing demands on materials properties. Homogeneity of raw materials has been improved by developing chemical synthetic methods such as sol-gel processing. Critical reaction conditions such as plasma CVD enable us to obtain novel compounds with special microstructures, although consuming much energy and producing unexpected exhausted materials. Recently, control of a reaction field in a non-equilibrium reaction is expected as an approach to synthesize novel materials and to control microstructure without excess energy and exhaustion. Sonochemical and mechanochemical synthesis have been developed to generate compounds which have difficulty to be synthesized in equilibrium reaction conditions, without excess energy (Fig.1). Some of relatively simple ceramic compounds have been synthesized by sonochemical and mechanochemical reaction[1)2)3)]. Destruction of cavity and mechanical compression of colliding balls promote non-equilibrium reaction, respectively. Extremely high pressure and high temperature condition which proceed a non-equilibrium reaction is caused by supply of ultrasonic irradiation and agitating grinding media.

In this paper, multiply of these non-equilibrium reactions to accelerate crystallization from precursor compounds was examined on the view point of topological modification of microstructure by the accumulation of excess internal energy.

$Ba_2YCu_3O_{7-y}$ (abbreviated as YBCO below) oxide superconductor was examined by adopting the mechanochemical-sonochemical concerted reaction on its multi-sequential condition-sensitive crystallization procedure .

2.EXPERIMENTAL

Precursor gel of YBCO superconductor was synthesized by sol-gel method using metal-acetates of each compounds. Synthesized gel was treated by mechanochemical reaction independently and combined with sonochemical reaction (Fig.2). Condition of each reaction was as follows; mechanochemical reaction was promoted by agitation of 0.5mm diameter balls at 115r.p.m. Sonochemical reaction was promoted by irradiation of ultrasonic wave with frequency of hundreds kHz and output power of 400W. Subsequently, treated precursor gels were heated up to the crystallization temperature of superconducting phase (680 ℃ in vacuum). Crystalline phase of treated and heated

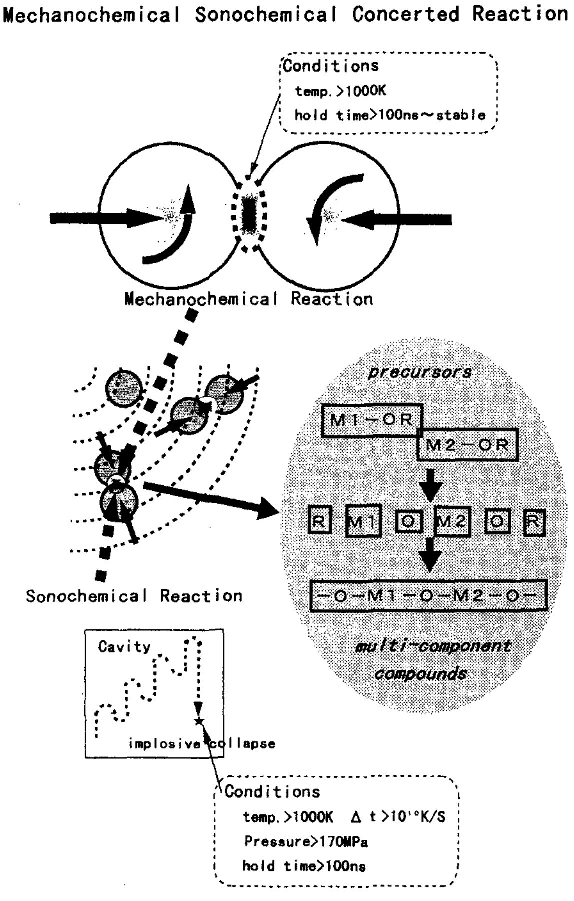

Figure 1: Scheme of mechanochemical-sonochemical concerted reaction and possible microstructure control in a bulk.

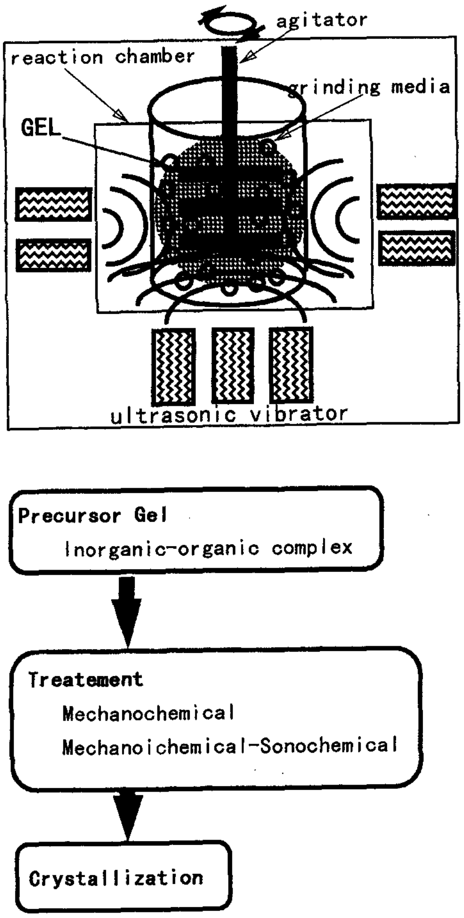

Figure 2: Scheme of the equipment and procedure of the concerted reaction.

precursor gel was evaluated by X-ray diffraction and high-temperature X-ray diffraction analysis. Microstructure of treated and heated precursor gels were observed by SEM and TEM. Compositional uniformity of treated and heated gels were examined by EDS analysis. Crystallization behavior was evaluated by DTA-TG and supported by spectroscopic analyses such as EELS, XPS and RAMAN.

3.RESULTS AND DISCUSSION

Mechanochemical treatment causes non-equilibrium reaction by addition of excess energy to a crystalline phase as sheared chemical bonding or torsion of crystal structure. Accumulation of internal energy cause enhancing a chemical reaction in some cases by activated chemical reaction potential remained in the system as dangling bond[3)4)]. Crystal strain accumulated as atomic displacement is also expected for a reaction accelerator through their relaxation process by supplying reaction energy in the system. On the other hand, unexpected phases often appear during relaxation process as the result of mismatching of additional energy with expected ordinary chemical reaction[5)6)]. For example, mechanical grinding of a precursor of $YBa_2Cu_3O_{7-y}$ superconductor (abbreviated as YBCO below) cause nanosize segregation of a crystallized compound composed of Cu and Y which is usually not recognized through ordinary reaction routes(Fig.3), even though the uniformity of elemental distribution in the precursor was improved by grinding. Mechanochemical treatment propose difficulty of optimumization at a reaction because of its extremely high pressure and temperature condition(see Fig.1) with regionally and timely restriction.

Sonochemical reaction has similar severe and

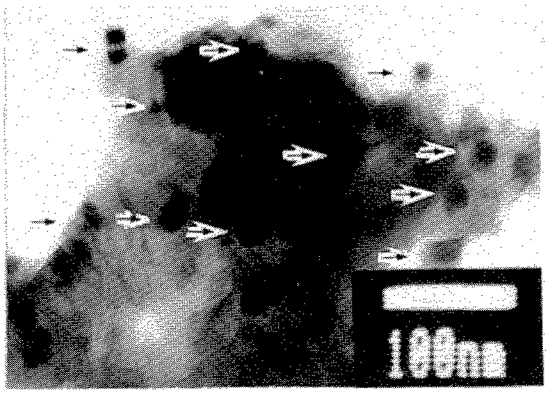

Figure 3: Segregation of Y-Cu oxide compound from a homogeneous precursor.

restricted condition for pressure, temperature and volume caused by implosive collapse of cavities generated by the irradiation of ultrasonic wave in an object. Non-equilibrium reaction in solution of the vapor-liquid-solid coexisting condition in micron size regions by the sonochemical reaction is available for some systems. Additionally, resonance of ultrasonic waves causes periodical distribution of high potential area for chemical reaction. Simultaneous overlapping of mechanochemical and sonochemical treatment is expected to cause synergistic reaction by coexisting of activation generated from different mechanisms. Furthermore, concerted reaction will be an approach for a possible microstructure control technique accompanied by the controlled reaction condition in the field(see Fig.1).

YBCO has layered perovskite crystal structure composed of multi-element. The superconducting phase crystallizes through the reaction of two-elements compounds crystallized by initial compounds of oxides and carbonates. For easier synthetic condition of YBCO crystallization, the compound resistive to thermal decomposition such as $BaCO_3$ should be avoided for its appearance through synthetic path. Calcination under vacuum condition promoting the decomposition of $BaCO_3$ just after its generation has been developed and resulted in decreasing crystallization temperature to the essentially requested one for YBCO crystallization.

Figure 4 shows crystallization of the precursor gel treated by mechanochemical-sonochemical concerted reaction and followed by heating up to 600℃. The result reveals direct crystallization of YBCO phase from amorphous precursor gel at the temperature 80℃ lower for mechanochemical-sonochemical concerted treatment than non-treated precursor. Advantage of concerted treatment compared with the precursor without treatment seems to be derived from additional internal energy accumulation in the precursor.

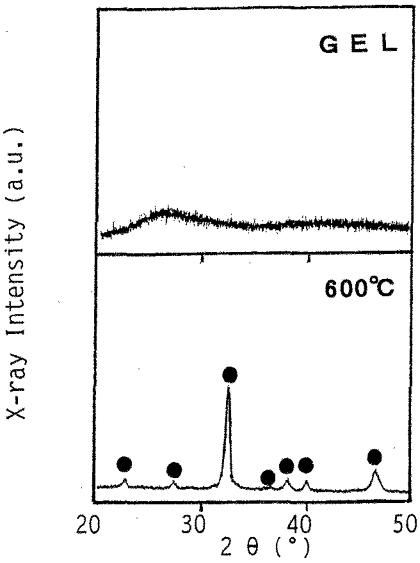

Figure 4: X-ray diffraction patterns indicating direct crystallization from amorphous gel through heat treatment.

The phenomena observed in the previous result for mechanochemically treated precursor gel[6], that is, the unexpected segregation of Y-Cu oxide from precursor through following heating caused by mechanochemical treatment singly was probably suppressed by the accumulation of internal energy, not simply as sheared chemical bonding but as a kind of reaction center for preferential crystallization of YBCO phase in it. TEM observation results supported the above speculation for the direct crystallization of YBCO phase from amorphous precursor gel after concerted treatment followed by heating up to 600℃. Figure 5 shows microstructure change of the precursor gel of mechanocemical-sonochemical concerted treatment through heat treatment. Amorphous uniform gel shows generation of self organized seeds in their matrix in its initial stage of crystallization. As the result of direct crystallization of YBCO from seeds, polycrystalline bulk of YBCO was obtained with random crystal growth direction through heating. No segregating phase between crystal grains was observed by high resolution TEM analysis.

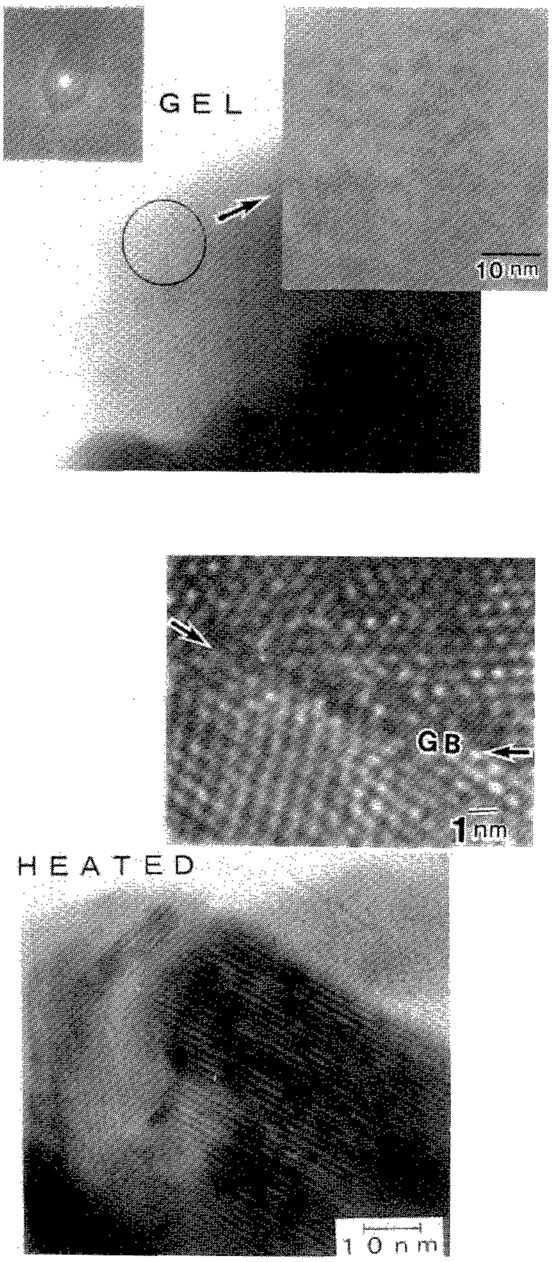

Figure 5: Microstructure of precursor gel and heat treated one after concerted treatment (TEM images).

The proposed procedure of YBCO crystallization at lower temperature was also supported by the DTA-TG analysis, high temperature X-ray diffraction analysis and spectroscopic analyses. DTA-TG curvature of the precursor gel after mechanochemical-sonochemical concerted treatment revealed the lack of the peak derived from crystallization of intermediate phases including $BaCO_3$. High temperature X-ray diffraction analysis also indicated the direct crystallization of YBCO from amorphous phase over 500℃.

4. CONCLUSIONS

Mechanochemical and sonochemical synthetic methods of precursors of YBCO superconductor was examined. Non-equilibrium reaction in the precursor by the mechanochemical and sonochemical concert reaction enable us to decrease the crystallization temperature of YBCO superconductor to 600℃. Microscopic observation and spectroscopic analyses indicated that the crystallization from in-situ formed nanosize seeds enhanced crystallization from the treated precursor through following heating, which resulted in the lower crystallization temperature.

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