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Metal oxide powder synthesized with amorphous metal chelates

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Chelate powder consisting of amorphous particles was synthesized through the process in which the droplet of the chelate solution is dried in the gas phase and solidified in a moment using a splay-dry technique. To investigate the advantage of the use of amorphous chelate powder in the processing of metal oxide powder, this study provides following two routes: a conventional route of mechanically mixing of crystalline metal-ethylenediaminetetraacetic acid (EDTA) powders and spray-dry mixing of metal-EDTA. These routes were followed by calcinations of metal-EDTA powder to form metal oxide powder. In this study, morphology, crystallization and metal composition of resulting (Ba,Sr)TiO_3 and $YBa_2Cu_3O_7$ powders were investigated. The amorphous metal-EDTA powder involving several metal elements is appropriate for successful calcination at lower temperatures rather than the mixture of crystalline powders prepared by mechanically mixing. *© 2002 Kluwer Academic Publishers*

1. Introduction

Powder of metal oxides is widely used capacitor dielectric, superconductor and phosphor because of their high performances, allowing the production of high capacitance devices and high luminescence devices within a small volume. An adequate degree of control of grain size and its distribution as well as metal composition is thus an important factor in the manufacture of metal oxide powder. A synthesis technique of metal oxide powder with the chelate complex, chelating technique, is widely proposed to control grain size of the powder. The chelate complex is an organic molecule that contains one metal ion in the structure and possesses mainly two advantages as the starting material in ceramic powder processing. One of them is low fraction of existence of powder contaminant element. The other is high ability of controlling of the metal composition. For example, Alcock *et. al.* [1] prepared $BaTiO_3$ powder using a co-precipitation processing route with metal ethylenediaminetetraacetic acid (EDTA). In this route, the co-precipitated powder prepared by solution chemistry was obtained using a peroxide route. This consisted of mixing a Ba^{2+}-EDTA complex solution with a Ti(IV) peroxy EDTA complex in measured proportions in the presence of an excess of hydrogen peroxide. Reaction between the Ba^{2+} and the titanium complex leads to the formation and precipitation of the Ba-Ti peroxy salt, $Ba[Ti(O_2)(OH)_4]$. In the powder obtained from calcination of $Ba[Ti(O_2)(OH)_4]$, less contaminations such as strontium, sulfur, phosphorus existed. Mratinex-Rubio *et al.* [2] synthesized $Y_2O_3:Eu$ powder using the chelating effect of EDTA. They obtained $Y_2O_3:Eu$ phosphor powder within a size ranging 20 to 60 nm. These powders still showed the luminescence efficiency around 60% of the larger standard materials.

A technique of the precipitation of EDTA has been widely known as that the chelate precipitation is obtained with gentle variation of pH in chelate solution. On the other hand, evaporation to dryness is also selected to synthesize chelate powder. These techniques are appropriate to form crystalline chelate powder. A spray-dray technique we proposed here is the method that the droplet of the chelate solution is dried in the gas phase in a moment. Because all metal chelates are solidified rapidly, the chelate particle consists of amorphous material.

When the chelate solution involves only one metal element, both amorphous and crystalline chelate particles can be used. However, if the solution involves two or more metal elements, the amorphous chelate particles are required to synthesize ceramic powder with good distribution of the metal composition. This is very important factor on controlling metal composition. As solubility of the metal chelate in water is strongly dependent on the kind of metal element, pH and temperature, the crystalline metal chelate involving more than two elements cannot exist with designated composition. On the other hand, the spray-dry technique solidifies the metal chelates in a moment. Fundamentally, the chelate particles are amorphous, therefore involves all metal elements as designated composition.

In this study, a detailed comparative evaluation has been carried out of two ceramic powder. One is the crystalline powder obtained from precipitation method followed by mixing and milling mechanically. The other is the amorphous powder made by the spray-dry method. The advantage of amorphous metal EDTA as the starting material in ceramic powder processing will be described and discussed.

2. Experimental

The following materials were used: EDTA · 2NH$_4$ (99.9%) is from Chubu Chelest, $SrCO_3$ (97.9%), $TiCl_4$ solution (20.6%), $BaCO_3$ (99.6%), $Y_2(CO_3)_3 \cdot 3H_2O$ (99.6%) and CuO (97.5%) were supplied by Kanto Chemical Co. The chelating procedure is explained using a example of EDTA · Sr · $(NH_4)_2$ synthesis. First, 0.6M EDTA · 2NH$_4$ was solved into deionized water followed by gentle stirred for 0.5 h at a temperature of 60°C. Next, the mixture of $SrCO_3$ and EDTA · 2NH$_4$ solution was stirred for 2 h at a temperature of 100°C. Furthermore, the solution was concentrated using an evaporator to form solution slurry. The slurry was cooled at the ambient temperature and stirred for 12 h. Finally, the crystal form of EDTA · Sr · $(NH_4)_2$ was obtained from the slurry using a centrifuge. Other crystalline chelates, EDTA · Ti · NH$_4$, EDTA · Ba · $(NH_4)_2$, EDTA · Y · $(NH_4)_2$ and EDTA · Cu · $(NH_4)_2$ were also synthesized same procedure.

In this experiment, a detailed comparative evaluation was carried of two types of the chelate mixture. One was produced by the conventional route of mixing, milling of crystalline chelate in an agate mortar, the other was made using spray-drying of chelate solution. A spray dryer with a double-fluid nozzle was employed in this experiment. A solution tank has a charging capacity of 3 L. The metal-EDTA solution is sprayed with a rate 300 mL/h, that produces metal-EDTA powder with a manufacturing speed of 50 g/h. To synthesize $SrTiO_3$ powder, equal molar quantity of EDTA · Sr · $(NH_4)_2$ and EDTA · Ti · NH$_4$ was mixed. For mechanical mixture, the sample was milled using the agate mortar for 1 h. On the other hand, to prepare chelate solution for the spray-dry method, EDTA · Sr · $(NH_4)_2$ and EDTA · Ti · NH$_4$ were solved into deionized water followed by gentle stirred for 0.5 h at pH 5–6. The mixture of solution was dried using a spray-dryer at a drying temperature of 160°C. Both Crystalline chelate and amorphous chelate are fired to continue chemical reaction using an air-opened electric furnace.

The unfired chelate and fired metal oxide powders were characterized using Fourier transform infrared spectroscopy (FTIR) with a Nicolet, IMPACT-410 and X-ray diffractometry with a Mac Science, M03XHF22. The metal composition of the unfired and fired powder was made using inductive coupled plasma-atomic emission spectroscopy (ICP-AES) with a Seiko Instruments, SPS-400. Scanning electron microscopy (SEM) was used to determine the particle size and morphology of the unfired chelate and fired metal oxide powders. The analysis was performed on a JEOL T-300. The average diameter of spherical particles was estimated from measuring approximately 200 particles per picture.

3. Results and discussion

3.1. Synthesis of $SrTiO_3$ and $(Ba,Sr)TiO_3$ powders

Two mixtures of two chelate reagents, EDTA · Ti · NH$_4$ and EDTA · Sr · $(NH_4)_2$ synthesized by two methods were examined by X-ray diffractometry, as shown in Fig. 1. Powders obtained using the precipitation technique showed clear diffraction lines that indicate chelate molecular crystals involving EDTA · Ti · NH$_4$ and EDTA · Sr · $(NH_4)_2$. On the other hand, the mixture obtained using the spray-dry technique showed no diffraction line. These results suggest that the mixture of EDTA · Ti · NH$_4$ and EDTA · Sr · $(NH_4)_2$ synthesized by the precipitation technique and the spray-dry technique are crystalline and amorphous, respectively.

The white samples were identified by FTIR spectroscopy as metal EDTA chelate in Fig. 2. From the spectra of crystalline and amorphous chelates, the following bands being indicative of the respective groups, 2500–3500 cm^{-1} CH$_2$, OH , NH and NH$_2$ stretch (ν), 1405 cm^{-1} CO ν_{as}, 1081 cm^{-1} ν_s, 753 cm^{-1} OHδ, and 680 cm^{-1} COδ. The broad absorption around 1620 cm^{-1} is due to the coordinated COOν. These absorptions suggest that the molecular structure exists in the mixed powder regardless of crystal or amorphous. The crystalline and amorphous unfired chelate powders showed a metal composition [Sr]/[Ti]of 1.00 on the ICP-AES results.

Fig. 3 indicates the SEM micrographs of the metal EDTA samples. The crystalline samples

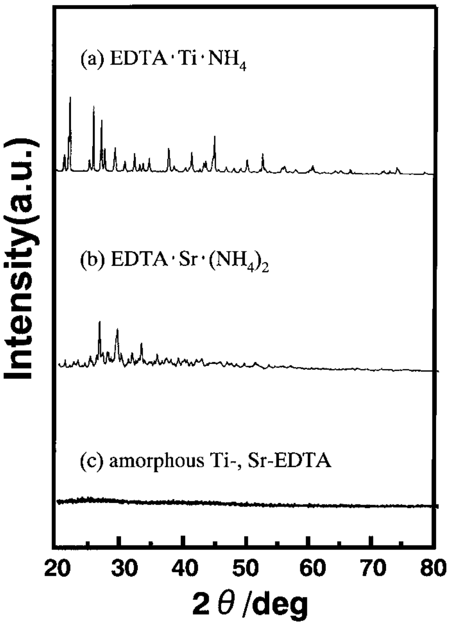

Figure 1 X-ray diffraction of starting EDTA powders.

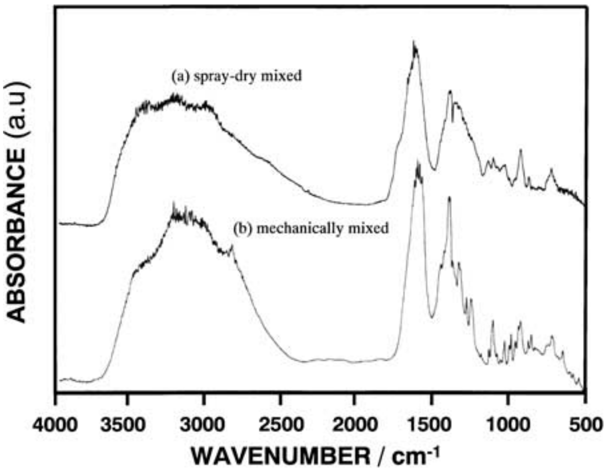

Figure 2 FTIR of starting EDTA powders.

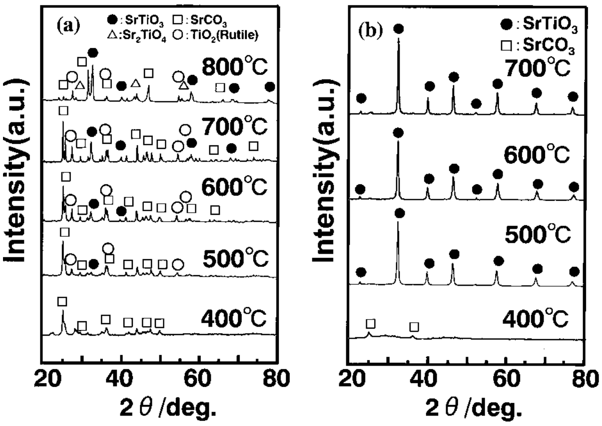

Figure 4 X-ray diffraction of resulting powders fired with (a) crystalline and (b) amorphous metal-EDTA.

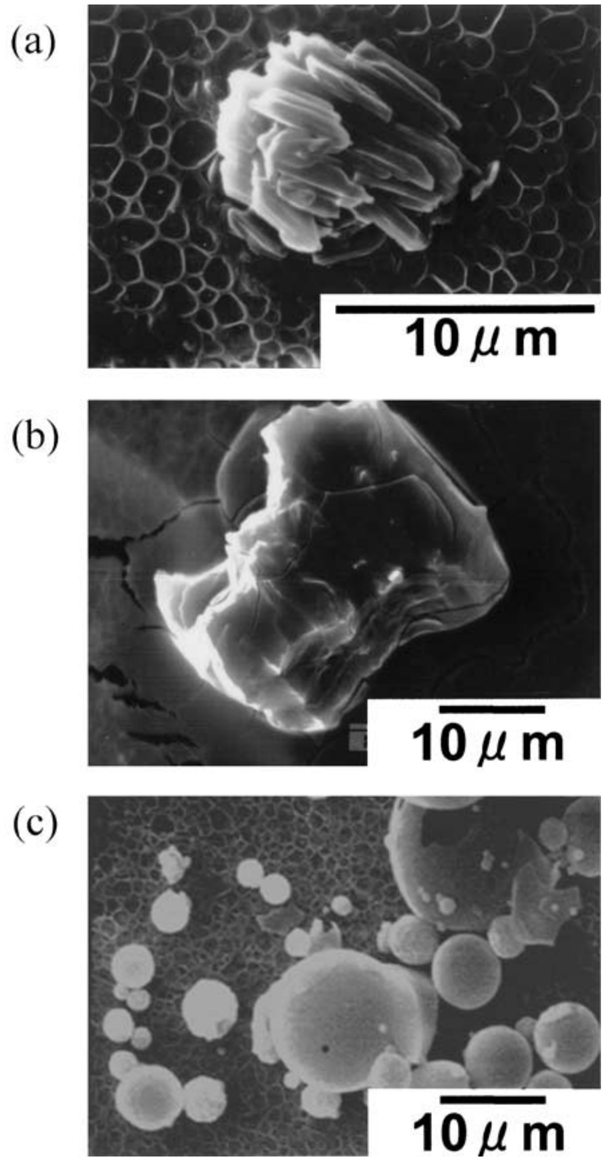

Figure 3 SEM micrographs of starting EDTA powders: (a) EDTA · Ti · NH_4, (b) EDTA · Sr · $(NH_4)_2$ and (c) amorphous Sr-, Ti-EDTA.

EDTA · Sr · $(NH_4)_2$ and EDTA · Ti · NH_4 showed characteristic morphology as the crystal with the average particle size of 15 μm and its distribution of 5–40 μm. On the other hand, the amorphous mixture consisted of sphere-like particles with the average particle size of 7 μm and its distribution of 0.5–15 μm. The size of crystalline chelate is too large to form nano-sized mixture using the agate mortar. On the other hand, it is strongly suggested that amorphous metal-EDTA possesses nano-sized mixture of EDTA · Ti · NH_4 and EDTA · Sr · $(NH_4)_2$

Fig. 4a is X-ray diffraction pattern of the samples fired at the temperatures of 400°C–800°C from the mixture of crystalline EDTA · Ti · NH_4 and EDTA · Sr · $(NH_4)_2$ particles. As metal EDTA is decomposed at the temperature ranging 300°C–400°C, the clear diffraction lines which are attributable to crystalline $SrCO_3$ were observed. With increasing the fired temperature, weak $SrTiO_3$, lines and clear TiO_2 (rutile structure) lines were seen at 500°C. The peak intensity of $SrTiO_3$ diffraction lines was increased with further firing. At 800°C, the peak intensity of $SrCO_3$ and TiO_2 diffraction lines were suddenly decreased, and then new lines attributable to Sr_2TiO_4 were observed. Finally, diffraction pattern was dominated by $SrTiO_3$, strontium rich Sr_2TiO_4 and rutile. On the other hand, Fig. 4b is X-ray diffraction pattern of the samples fired at the temperatures of 400°C–800°C from the mixture of amorphous EDTA · Ti · NH_4 and EDTA · Sr · $(NH_4)_2$ particles. Although, the clear diffraction lines which are attributable to crystalline $SrCO_3$ were observed, very strong $SrTiO_3$ (110), (111), (200), (211) and (220) lines were seen over 500°C. No diffraction lines attributed to other materials were obtained.

The thermal decomposition reactions of EDTA · Ti · NH_4 and EDTA · Sr · $(NH_4)_2$ chelates are written by two equations.

$$\begin{aligned}2\mathrm{EDTA}\cdot\mathrm{Sr}\cdot(\mathrm{NH_4})_2 + 31\mathrm{O_2} &\rightarrow 2\mathrm{SrCO_3}\\ &+ 18\mathrm{CO_2} + 20\mathrm{H_2O} + 8\mathrm{NO_2}, \qquad (1)\end{aligned}$$

$$\begin{aligned}2\mathrm{EDTA}\cdot\mathrm{Ti}\cdot\mathrm{NH_4} + 28\mathrm{O_2} &\rightarrow 2\mathrm{TiO_2}\\ &+ 20\mathrm{CO_2} + 16\mathrm{H_2O} + 6\mathrm{NO_2}. \qquad (2)\end{aligned}$$

Two reactions (1) and (2) are followed by the reaction between $SrCO_3$ and TiO_2. However, the final product is strongly influenced by conditions of starting chelate powder. The reaction route started from the crystalline metal-EDTA particle forms the crystalline grains of

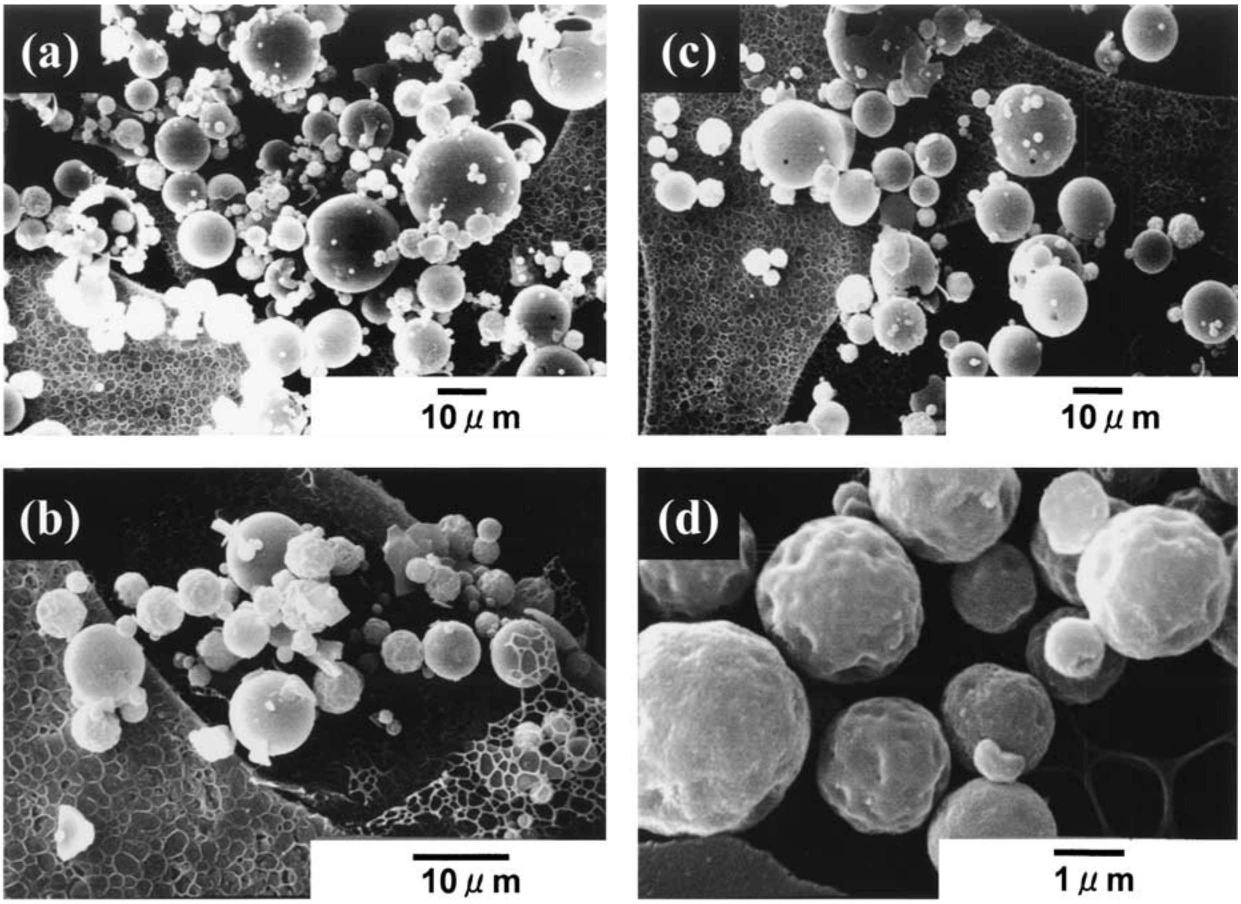

Figure 5 SEM micrographs of resulting powders fired at (a) 400°C, (b) 450°C, (c) 500°C and (d) 700°C.

$SrCO_3$ and TiO_2. The grain size might be in sub-micron meters. In this case, the crystalline grains of $SrCO_3$ and TiO_2might be larger than the diffusion distance of Sr and Ti atoms for firing duration. The reaction proceeds with the Equation 3.

$$2SrCO_3 + TiO_2 \rightarrow Sr_2TiO_4 + 2CO_2 \tag{3}$$

On the other hand, the reaction route started from the amorphous metal-EDTA particle forms possibly the nano-sized grains of $SrCO_3$ and TiO_2. In this case, the nano-sized grains of $SrCO_3$ and TiO_2should be smaller than the diffusion distance of Sr and Ti atoms for firing duration. The reaction proceeds with the Equation 4.

$$SrCO_3 + TiO_2 \rightarrow SrTiO_3 + CO_2 \tag{4}$$

At high temperature conditions, $SrTiO_3$ is formed directly. The reaction (5) proceeds.

$$\begin{aligned} &2\mathrm{EDTA}\cdot\mathrm{Sr}\cdot(\mathrm{NH_4})_2 + 2\mathrm{EDTA}\cdot\mathrm{Ti}\cdot\mathrm{NH_4} + 59\mathrm{O_2} \\ &\quad\rightarrow \mathrm{SrTiO_3} + 40\mathrm{CO_2} + 36\mathrm{H_2O} + 14\mathrm{NO_2}. \end{aligned} \tag{5}$$

The results of X-ray diffraction imply that the use of spray-dry powder has advantage for low temperature firing of processing of metal oxide powder.

Fig. 5 indicates the SEM micrographs of the resulting powder obtained with spray-dried metal-EDTA samples. The average particle size and its distribution were 4 μm and 0.5–13 μm. The particle size was independent upon the fired temperature. The smooth surface before firing changed to rough surface after firing. Several craters were seen on the surface, suggesting the volume reduction of the particles. These powders showed a stoichiometric metal composition [Sr]/[Ti]of 1.00 on the ICP-AES results.

X-ray diffraction patterns of the $(Ba,Sr)TiO_3$ powders deposited at the substrate temperatures of 500–700°C were measured. The [Ba]/([Ba] + [Sr]) ratios of 0.2, 0.4 and 0.6 were selected for the metallic composition in the starting amorphous chelates. (110), (111), (200), (211) and (220) peaks were observed as the diffraction lines that were attributable to $(Ba,Sr)TiO_3$ phase. The lattice constant a_0 of $(Ba,Sr)TiO_3$ phase was strongly dependent upon the Ba/(Ba+Sr) ratio, as shown in Fig. 6. The lattice constant a_0 was calculated from all the peaks appeared on the diffraction

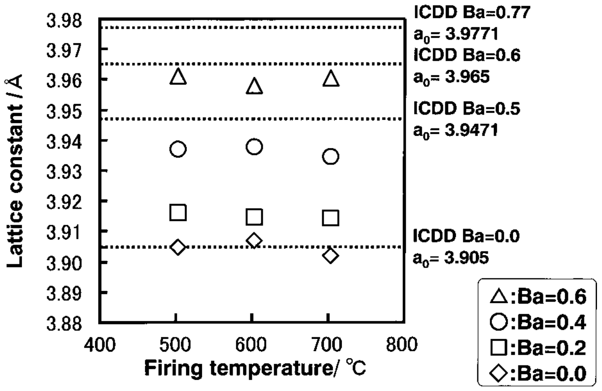

Figure 6 Lattice constant of $Ba_xSr_{1-x}TiO_3$ fired at various temperatures with amorphous metal-EDTA.

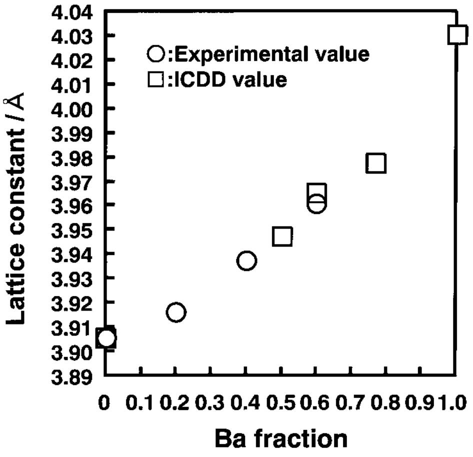

Figure 7 Lattice constant of $Ba_xSr_{1-x}TiO_3$ with various Ba fractions in starting EDTA.

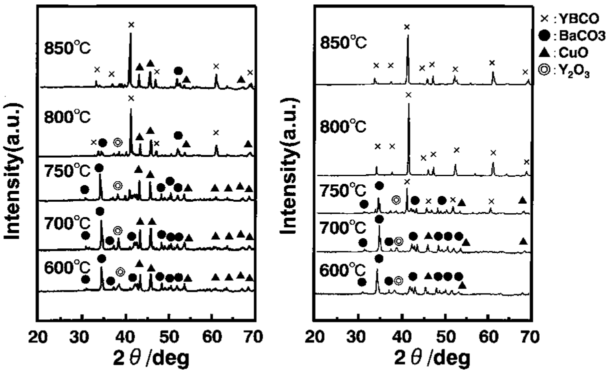

Figure 8 X-ray diffraction of resulting powders fired with (a) crystalline and (b) amorphous metal-EDTA.

pattern. The lattice constant increased with increasing the [Ba]/([Ba] + [Sr]) ratio. This result implies that this technique is appropriate for composition design of metal oxide particles with complicated metallic composition.

It is well known that Vegard role [3] increases the lattice constant with increasing the Ba fraction in $(Ba,Sr)TiO_3$. The open-square symbols in Fig. 7 indicates the International Center for Diffraction Data (ICDD) card data of $(Ba,Sr)TiO_3$ with the [Ba]/([Ba] + [Sr]) ratio of 0, 0.5, 0.6 and 0.77, showing Vegard role. The open-circle symbols are represent the results obtained here. The results suggest that the metal composition is well controlled.

3.2. Synthesis of $YBa_2Cu_3O_7$ powder

Fig. 8a is X-ray diffraction pattern of the samples fired at the temperatures of 400°C–850°C from the mixture of crystalline $EDTA \cdot Y \cdot (NH_4)_2$, $EDTA \cdot Ba \cdot (NH_4)_2$ and $EDTA \cdot Cu \cdot (NH_4)_2$ particles. The clear diffraction lines which were attributable to crystalline Y_2O_3, $BaCO_3$ and CuO were observed. With increasing the firing temperature, weak $YBa_2Cu_3O_7$ lines were observed addition to the Y_2O_3, $BaCO_3$ and CuO lines. On the other hand, Fig. 8b is X-ray diffraction pattern of the samples fired at the temperatures of 600°C–850°C from the mixture of amorphous $EDTA \cdot Y \cdot (NH_4)_2$, $EDTA \cdot Ba \cdot (NH_4)_2$ and $EDTA \cdot Cu \cdot (NH_4)_2$ particles. At a temperature of 800°C, very strong $YBa_2Cu_3O_7$ lines were seen. No diffraction lines attributed to other materials were obtained.

The thermal decomposition reactions of $EDTA \cdot Y \cdot (NH_4)_2$, $EDTA \cdot Ba \cdot (NH_4)_2$ and $EDTA \cdot Cu \cdot (NH_4)_2$ chelates are written by three equations.

$$4EDTA \cdot Y \cdot (NH_4)_2 + 33O_2 \rightarrow 2Y_2O_3 + 20CO_2 + 20H_2O + 16NO_2, \tag{6}$$

$$2EDTA \cdot Ba \cdot (NH_4)_2 + 31O_2 \rightarrow 2BaCO_3 + 18CO_2 + 20H_2O + 8NO_2, \tag{7}$$

$$2EDTA \cdot Cu \cdot (NH_4)_2 + 31O_2 \rightarrow 2CuO + 20CO_2 + 20H_2O + 8NO_2. \tag{8}$$

Three reactions (6)–(8) are followed by the reaction of Y_2O_3, $BaCO_3$ and CuO. However, the final product is also strongly influenced by conditions of starting chelate powder. This process proceeds by similar route with $SrTiO_3$ reaction. Therefore, in this route the amorphous metal EDTA particle is also advantageous to form $YBa_2Cu_3O_7$ structure.

4. Conclusion

The advantage of amorphous metal EDTA as the starting material of ceramic powder processing is described and discussed. The amorphous metal EDTA powder involving several metal elements sinters overall much lower temperature than the powder prepared mechanically mixing. The results of synthesis of $(Ba,Sr)TiO_3$ powder with variation of Ba fraction suggest that the metal composition is well controlled.

Acknowledgement

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