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Preparation of nanosized Gd_2CuO_4 cuprate using amorphous heteronuclear complex as a precursor at low temperature

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Nanosized Gd_2CuO_4 cuprate oxide was prepared at a low temperature using an amorphous heteronuclear complex, $Gd_2Cu(DTPA)_{1.6}\cdot 6H_2O$, as a precursor. DTA and TGA indicated that the precursor can be completely decomposed above 500 °C. XPS indicated the decomposition product consisted of Gd_2CuO_4 cuprate oxide after the precursor was calcined at 500 °C for 2 h. XRD demonstrated that the nanosized crystalline Gd_2CuO_4 cuprate was formed after the calcination temperature increased to 600 °C. TEM showed that the particle size of Gd_2CuO_4 cuprate increased from 20 to 50 nm when the calcination temperature increased from 500 to 800 °C, and the particle size increased from 10 to 30 nm when the precursor was calcined at 500 °C from 1 to 8 h. © *1999 Kluwer Academic Publishers*

1. Introduction

Since the discovery of the doped superconductors $R_{1.85}M_{0.15}CuO_4$ (R = Pr, Nd, Sm, or Eu, M = Ce, Th) [1, 2], much attention has been paid to the preparation, the structures and the properties of the undoped materials such as R_2CuO_4 [3]. Gd_2CuO_4 cuprate also attracts many researchers due to its special structure and properties [4, 5]. Gd_2CuO_4 cuprate has been prepared in several ways. It can be synthesized by solid state reaction using Gd_2O_3 and CuO oxides at 1050 °C, or by a co-precipitate technique at 650 °C [6]. The particle size of Gd_2CuO_4 material strongly effects on the dynamic magnetic behaviors [7–9]. It is very important to find a new method of preparing nanosized Gd_2CuO_4 cuprate powder and thin film.

The complicated ceramic oxides have application in opto-electronics, megneto-optics, superconductivity, electrode and sensor materials, and catalysis [10–13]. It is very important how to prepare nanosized complicated ceramic oxides. Although the sol-gel method has been widely used to prepare nanosized ceramic oxide, the application of the sol-gel method for complicated oxide is still limited due to the limitation of chemical regents. Because amorphous heteronuclear complexes can form thin film and be decomposed at relatively low calcination temperature [14], we attempt to prepare nanosized cuprate oxide using an amorphous heteronuclear complex as a precursor.

The amorphous complex precursors are $GdCu(DTPA)\cdot 6H_2O$ and $Gd_2Cu(DTPA)_{1.6}\cdot 6H_2O$. The decomposition temperatures of these two precursors were 410 and 500 °C, respectively. The Gd_2CuO_4 cuprate oxide was obtained after the precursor was calcined at 500 °C for 2 h, and the crystalline Gd_2CuO_4 phase was formed after calcined at 600 °C for 2 h. The crystalline size increased from 20 to 50 nm when the calcination temperature increased from 500 to 800 °C, and the particle size increased from 10 to 30 nm when the precursor was calcined at 500 °C from 1 to 8 h. It is a useful method to synthesize nanosized cuprate oxide using the amorphous heteronuclear complex as a precursor.

2. Experimental details

2.1. The synthesis of $Gd_2Cu(DTPA)_{1.6}\cdot 6H_2O$ and $GdCu(DTPA)\cdot 6H_2O$ precursor

The fresh $Gd(OH)_3$ and $Cu(OH)_2$ powders were prepared by the reaction between $Gd(NO_3)_3$ and $Cu(NO_3)_2$ and NaOH solution, respectively. The complex precursors were synthesized by the reaction of Diethylenetriaminepentaacetic acid (H_5DTPA) and fresh $Gd(OH)_3$, $Cu(OH)_2$ in water with calculated molar ratio. The

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mixture was stirred and heated until all solid powder dissolved completely. After the mixture became a transparent solution, it was vaporized slowly at room temperature until a piece of transparent glass formed. The result of element analysis showed that the possible formula of these two kinds of precursors were $Gd_2Cu(DTPA)_{1.6}\cdot 6H_2O$ and $GdCu(DTPA)\cdot 6H_2O$. XRD and electron diffraction demonstrated that both complex precursors were amorphous.

2.2. The preparation of Gd_2CuO_4 cuprate oxide

The Gd_2CuO_4 cuprate oxide was prepared by calcination of the complex precursor in air. At first, the temperature increased to 400 °C at a slow heat rate (10 °C/min). Then, the temperature was maintained at 400 °C for 30 min to promote the decomposition of organic composition. Finally, the temperature increased to various pre-set temperatures and maintained at a definite time to promote the formation of cuprate oxide.

2.3. Experimental techniques

XRD experiments were caried out in Rigako DMAX-2400 diffractometer with Cu anode. The topography and particle size were measured using a Hitachi H-800 Transmission Electron Microscopy (TEM). The accelerating voltage of electron beam was 200 kV. TGA and DTA were performed on a Dupond 1090 thermal analyzer. The atmosphere was air, and the heat rate was 10 °C/min. The XPS spectra were measured in a PHI 5300 ESCA system. A MgK_α X-ray source with a power of 250 W was used. The pass energy of the analyzer was set at 37.25 eV and the base pressure of the vacuum chamber was better than 3×10^{-9} torr. The charge effect was calibrated using the binding energy of C 1s [15].

3. Results and discussion

3.1. The thermal decomposition

The thermal analysis results of TGA for $GdCu(DTPA)\cdot 6H_2O$ complex are shown in Fig. 1. The solid curve shows the residual weight change (TG) with temperature and the dot curve shows the derivative of the weight change (DTG). The TG curve indicated that the increase of temperature resulted in five different regions of weight loss. These regions corresponded to five weight derivative peaks on the DTG curve. According to quantitative calculation of the weight loss in every region, the thermal decomposition processes can be distinguished as followings. The weight loss peak at 56.8 °C resulted from the loss of coordinated water. The peaks at 235.7 and 287.1 °C resulted from the decomposition of CH_x organic component and the decomposition of amino-group, respectively. The strong weight loss peaks at 390.0 and 424.2 °C were produced by the decomposition of carboxyl copper group and the decomposition of carboxyl gadolinium group. The decomposition temperature of the carboxyl copper group and the carboxyl gadolinium group was similar, which was helpful to promote the formation of cuprate oxide.

The TGA and DTA spectra of $Gd_2Cu(DTPA)_{1.6}\cdot 6H_2O$ are shown in Fig. 2. The TGA curve of $Gd_2Cu(DTPA)_{1.6}\cdot 6H_2O$ was similar to that of $GdCu(DTPA)\cdot 6H_2O$ complex. But, the weight loss regions were overlap, and the decomposition of amino-group and CH_x organic component can not be distinguished clearly. The decomposition regions became wide and the decomposition temperature increased. The completely decomposition temperature of $Gd_2Cu(DTPA)_{1.6}\cdot 6H_2O$ precursor was 560 °C, which was much higher than that of $GdCu(DTPA)\cdot 6H_2O$ (430 °C), implying that the Gd_2CuO_4 complicated oxide can form at much lower temperature using $GdCu(DTPA)\cdot 6H_2O$ than using $Gd_2Cu(DTPA)_{1.6}\cdot 6H_2O$ as precursor. Three exothermic peaks were found on the DTA curve. The peak at 271.6 °C was produced by the burning of CH_x and amino-group, and the peak at 407.3 °C was produced by the decomposition of carboxyl copper group. The peak at 489.4 °C was very strong, which contained both exothermic contribution from the decomposition of carboxyl gadolinium group and the formation of Gd_2CuO_4 complicated oxide. Because the exothermic heat of

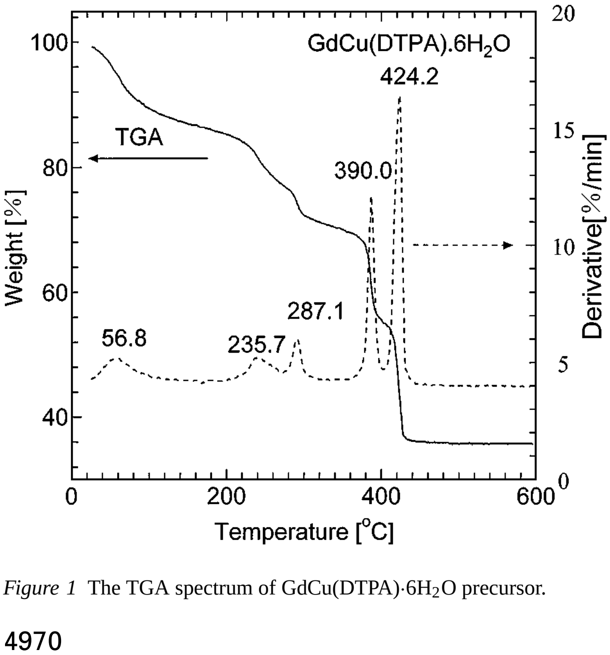

Figure 1 The TGA spectrum of $GdCu(DTPA)\cdot 6H_2O$ precursor.

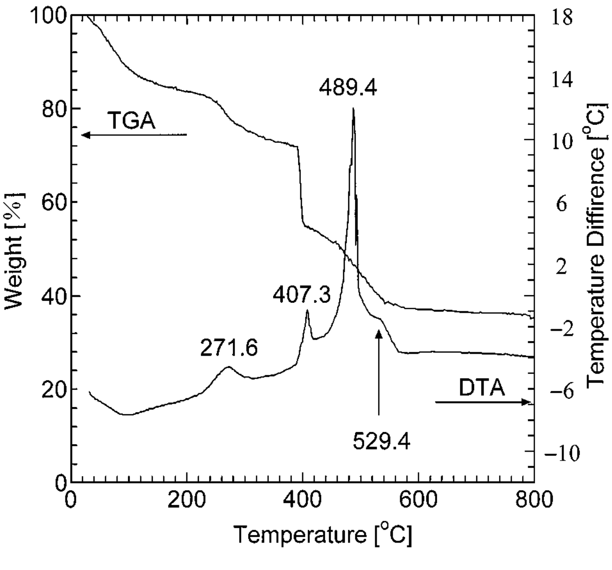

Figure 2 The TGA and DTA spectra of $Gd_2Cu(DTPA)_{1.6}\cdot 6H_2O$ precursor.

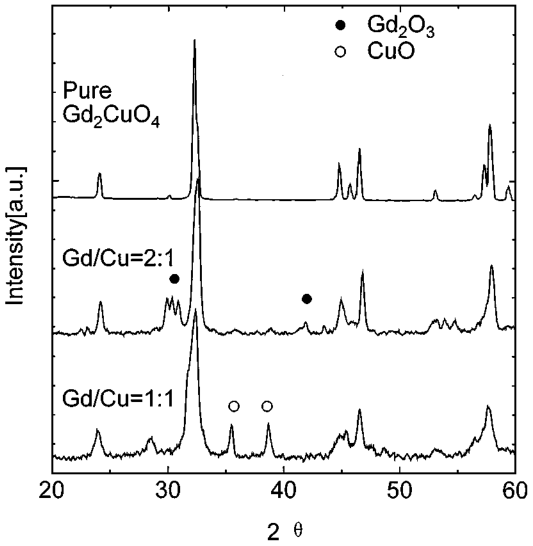

Figure 3 The XRD patterns of calcined species using $Gd_2Cu(DTPA)_{1.6}\cdot 6H_2O$ and $GdCu(DTPA)\cdot 6H_2O$ precursors.

carboxyl group was small, most exothermic heat came from the formation of cuprate. The shoulder peak at 529.4 °C resulted from the crystallization of Gd_2CuO_4. The above results suggest that Gd_2CuO_4 cuprate oxide can be formed below 500 °C by decomposing an amorphous complex.

3.2. The crystallization of Gd_2CuO_4 compound

The formation of Gd_2CuO_4 crystalline phase has been investigated using XRD. Fig. 3 shows the XRD patterns of decomposition species from these two precursors. The major decomposition phase for these two precursors was crystalline Gd_2CuO_4. A second phase was found in both decompositions. A small amount Gd_2O_3 phase and a considerable amount of CuO phase existed in the decomposition product from $Gd_2Cu(DTPA)_{1.6}\cdot 6H_2O$ and $GdCu(DTPA)\cdot 6H_2O$ precursors, respectively. In $GdCu(DTPA)\cdot 6H_2O$ precursor, the ratio of Gd/Cu was 1 : 1, meaning that there was 50% excess Cu in the precursor, thus, the CuO phase formed after the precursor was calcined. In the $GdCu(DTPA)\cdot 6H_2O$ precursor, the ratio of Gd/Cu is 2 : 1, stoichiometric for a Gd_2CuO_4 cuprate. A small amount of Gd_2O_3 was still detected after the precursor was calcined at 800 °C for 2 h. It may result from extra Gd in the precursor. In addition, the Gd_2CuO_4 crystalline phase can be formed at 600 °C for 2 h using $GdCu(DTPA)\cdot 6H_2O$ as the precursor. The calcination temperature must increase to 700 °C to obtain the crystalline cuprate using $Gd_2Cu(DTPA)_{1.6}\cdot 6H_2O$ as the precursor. This can be explained from the TGA result, which indicated that the decomposition temperature of $GdCu(DTPA)\cdot 6H_2O$ was much lower than that of $Gd_2Cu(DTPA)_{1.6}\cdot 6H_2O$. Above results suggested that Gd_2CuO_4 cuprate oxide can be formed from these precursors with various Gd/Cu ratio.

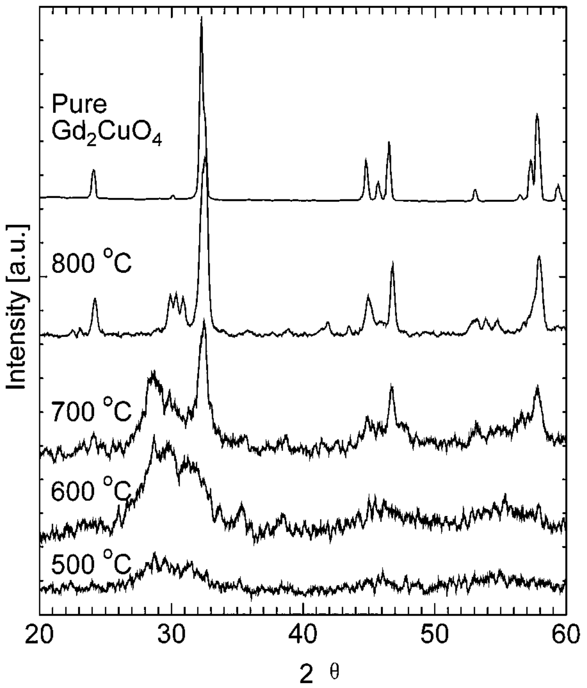

Figure 4 The XRD patterns of decomposed product varied in calcination temperature.

The XRD patterns of Gd_2CuO_4 crystalline phase in different calcination temperatures are shown in Fig. 4. XRD demonstrated that the Gd_2CuO_4 phase was amorphous when the calcination temperature was 500 °C. After the calcination temperature increased to 600 °C, several broad peaks appeared, implying the formation of Gd_2CuO_4 crystalline phase. This result was confirmed by electron diffraction, which showed the polycrystalline diffraction pattern. After the calcination temperature increased to 700 °C, the sharp peaks of a crystalline Gd_2CuO_4 phase appeared in the XRD pattern. After the sample was calcined at 800 °C for 2 h, the XRD pattern was similar to a standard pattern of Gd_2CuO_4. Electron diffraction also found the existence of crystalline Gd_2CuO_4. The above results indicate Gd_2CuO_4 crystalline phase can be formed at relatively low temperature using an amorphous complex as a precursor.

3.3. The identification of Gd_2CuO_4 cuprate oxide

The chemical composition of decomposed precursor has been determined using XPS. The Cu 2p spectra in decomposed samples calcined at different temperatures are shown in Fig. 5. This figure showed that the binding energies of Cu $2p_{3/2}$ in pure copper and CuO were 932.4 and 933.6 eV, respectively. The binding energy of Cu $2p_{3/2}$ in decomposed precursor was 932.8 eV, which was higher than that in pure Cu and lower than that in CuO, meaning that Cu did not exist as either CuO species or pure copper in decomposed precursor. The line shape of Cu 2p in decomposed species was different from that in CuO and Cu_2O compounds, and it was closed to that in pure copper. From the results of Cu 2p, it can be considered that Cu existed as the cuprate oxide in decomposed product, implying that the precursor has decomposed into Gd_2CuO_4 cuprate oxide after treated at 500 °C for 2 h. The shake-up peaks of Cu 2p in decomposed product at low calcination

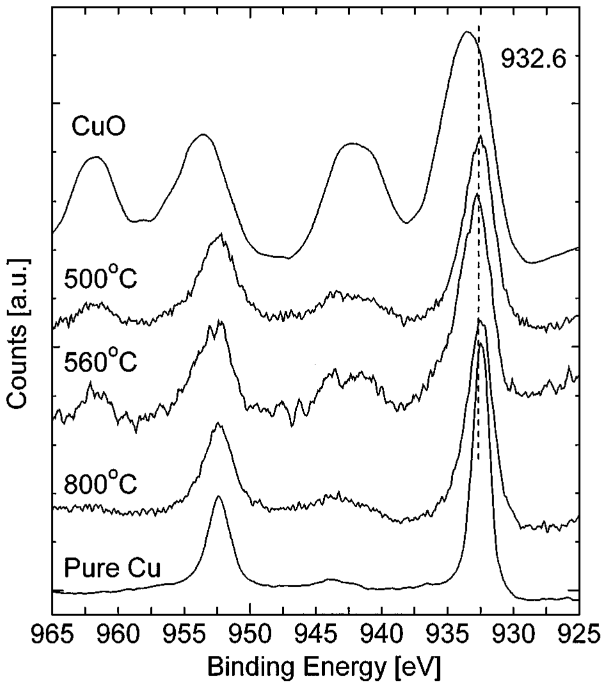

Figure 5 The Cu 2p spectra of decomposed product in various calcination temperatures for 2 h.

temperature were much stronger, and decreased with the increase of calcination temperature, suggesting that the shake-up peak resulted from carboxyl copper.

When the calcination temperature was 500 °C, there were two peaks in C 1s spectrum. The binding energies were 284.8 and 289.4 eV, which can be attributed to carbonized carbon and carboxyl group, respectively. The existence of carbonized carbon indicated that the organic carbon can not be oxidized completely at 500 °C, and the existence of carboxyl group implied that the precursor did not decompose completely at 500 °C for 2 h. With the increase of calcination temperature, the peak at 289.4 eV disappeared gradually, suggesting that the decomposition of carboxyl group was promoted by increasing the calcination temperature. According to the quantitative XPS analysis, the amount of carbonized carbon decreased dramatically with increasing calcination temperature.

The XPS results of Gd 4d spectra indicated that the binding energies in decomposed sample calcined at different temperature were similar (141.4 eV). The binding energies of Gd 4d in pure Gd and Gd_2O_3 compounds were 140.4 and 143.6 eV, respectively [15]. The binding energy of Gd 4d in decomposed species treated at 500 °C for 2 h was 141.2 eV, suggesting that the decomposed product was cuprate oxide. With the increase of calcination temperature from 500 to 800 °C, the binding energy of Gd 4d maintains at 141.4 eV, suggesting that Gd existed as Gd_2CuO_4 cuprate oxide at decomposed products, which were calcined at a temperature range of 500 to 800 °C.

3.4. The particle size of Gd_2CuO_4 species

The varieties of particle size of Gd_2CuO_4 cuprate with calcination temperature have been studied using TEM. TEM showed that the particle size of Gd_2CuO_4 compound was very small and homogenous even though the sample was calcined at 700 °C for 2 h. The particle size was closed to 30 nm. EDAX indicated that the ratio of Gd/Cu in these particles was near to 2 : 1, which was consistent with the ratio of Gd/Cu in Gd_2CuO_4 cuprate. Electron diffraction also showed that some particles consisted of single crystal of Gd_2CuO_4.

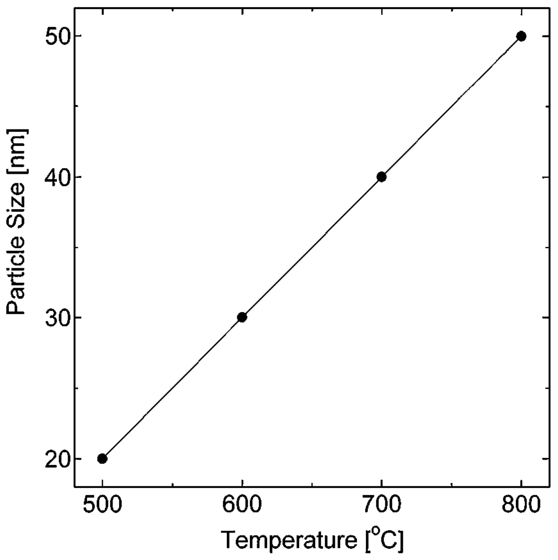

Figure 6 The relationship of particle size and the calcination temperature.

The effect of calcination temperature on particle size is shown in Fig. 6. All samples were calcined at definite temperature for 2 h. After the precursor was calcined at 500 °C, the particle size was about 20 nm. When the calcination temperature increased to 800 °C, the particle size reached at 50 nm. Fig. 8 showed that the particle size linearly increased with increasing calcination temperature.

The calcination time also affected the particle size of Gd_2CuO_4 compound. Fig. 7 shows the effects of calcination time on the particle size. After the precursor calcined at 500 °C for 1 h, the particle size was about 10 nm. When the calcination time prolonged to 8 h, the

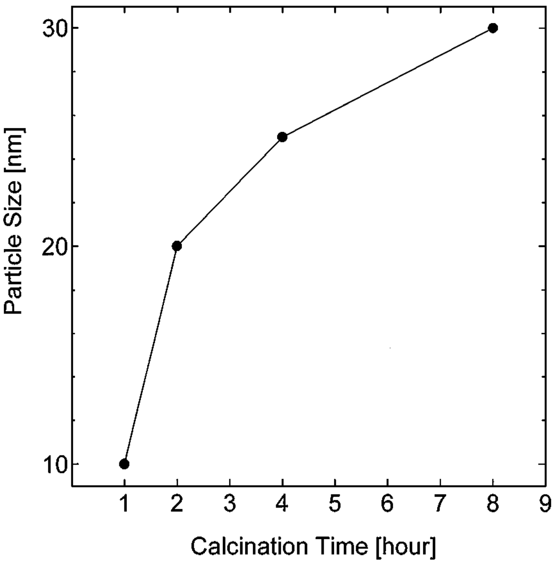

Figure 7 The relationship of particle size and the calcination time.

particle size increased to 30 nm. The effect of calcination time on particle size displayed a hyperbola distribution, implying that the particle size would reach an asymptotic valve when the calcination time was enough long. The functional relationship of calcination time and temperature on particle size was different.

4. Conclusion

1. The nanosized Gd_2CuO_4 complicated oxide was synthesized using amorphous heteronuclear complex as a precursor at relatively low calcination temperature.
2. To form crystalline Gd_2CuO_4 phase, the calcination temperature should be above 600 °C using $Gd_2Cu(DTPA)_{1.6}\cdot 6H_2O$ as a precursor.
3. The particle size was still in nano scale even if the calcination temperature increased to 800 °C.

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