CHAPTER 3

EXPERIMENTAL PROCEDURES

3.1. Ceramic processing of $CaCu_3Ti_4O_{12}$

3.1.1 Chemical compositions

Table 3.1 Starting materials for modified $CaCu_3Ti_4O_{12}$ ceramics.

Oxide	Manufacturer	Purity
$CaCO_3$	Fisher	99.0%
CuO	Alfa Aesar	99.0%
TiO_2	Fisher	98.0 - 100.5%
MnO_2	Aldrich	99.0%
ZrO_2	Riedel-de Haën	99.0%
CeO_2	Aldrich	99.0%
GeO_2	Alfa Aesar	99.98%
Cs_2CO_3	Aldrich	99.9%
In_2O_3	Alfa Aesar	99.9%

In the mixing process, the calculated relevant proportions of constituents were weighed according to formulae below

$CaCu_3Ti_4O_{12}$, (CCTO):

$$CaCO_3 + 3CuO + 4TiO_2 \longrightarrow CaCu_3Ti_4O_{12} + CO_2\ (g)$$

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3.1.2. Batching, mixing, and milling processes

In order to carry out the research on copper calcium titanate, a variety of bulk ceramic samples of $CaCu_3Ti_4O_{12}$ have been manufactured by utilizing traditional methods of solid state synthesis. First, the following three oxide powders were prepared: 1) calcium carbonate ($CaCO_3$); 2) copper (II) oxide (CuO); 3) Titanium (IV) oxide (TiO_2). Based on the chemical stoichiometry of Ca:Cu:Ti:O as 1:3:4:12, the weight of each oxide powder was obtained and measured by batch calculation in order to produce the stoichiometric compound of $CaCu_3Ti_4O_{12}$. The stoichiometry of $CaCu_3Ti_4O12$ was modified when the dopants of MnO_2, CeO_2, ZrO_2, GeO_2, and Cs_2CO_3 were added. After certain amounts of cylindrical shaped yttria-stabilized zirconia media were inserted into a Nalgene bottle, the measured powders were then added into the bottle. To mix those different powders homogeneously, the measured volume of ethyl alcohol was added and the bottle was put into the vibratory mill (M-18 grinding mill, SWECO Inc., Florence, KY), shown in Figure 3.1, for 6 hours. After the milling process was finished, the mixture of powders and ethyl alcohol was separated from the media and was collected in the evaporation dish. Then, the dish was dried overnight in the drying chamber at 150 ^{o}F.

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Figure 3.1 Photo image of a vibratory mill (SWECO M-18 grinding mill)

3.1.3. Calcination process

In spite of using high purity powders refined by the chemical processes from the manufacturing companies, there exist certain amounts of impurities after the milling and drying processes. To reduce these impurities and obtain the homogeneity of the final compound of $CaCu_3Ti_4O_{12}$, the dried powder consisting of $CaCO_3$, CuO, and TiO_2 was heated up to the high temperature. For the current research of $CaCu_3Ti_4O_{12}$, the calcination was performed at 900 ^oC for 6 hours followed by furnace cooling. The detailed processing schedule is shown in Figure 3.2. The hard agglomerates after the calcination was then pulverized in a mortar first, moved to the

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vibratory mill for 6 hours of running, and dried in the drying chamber to obtain the powders of $CaCu_3Ti_4O_{12}$ with the reduced particle size.

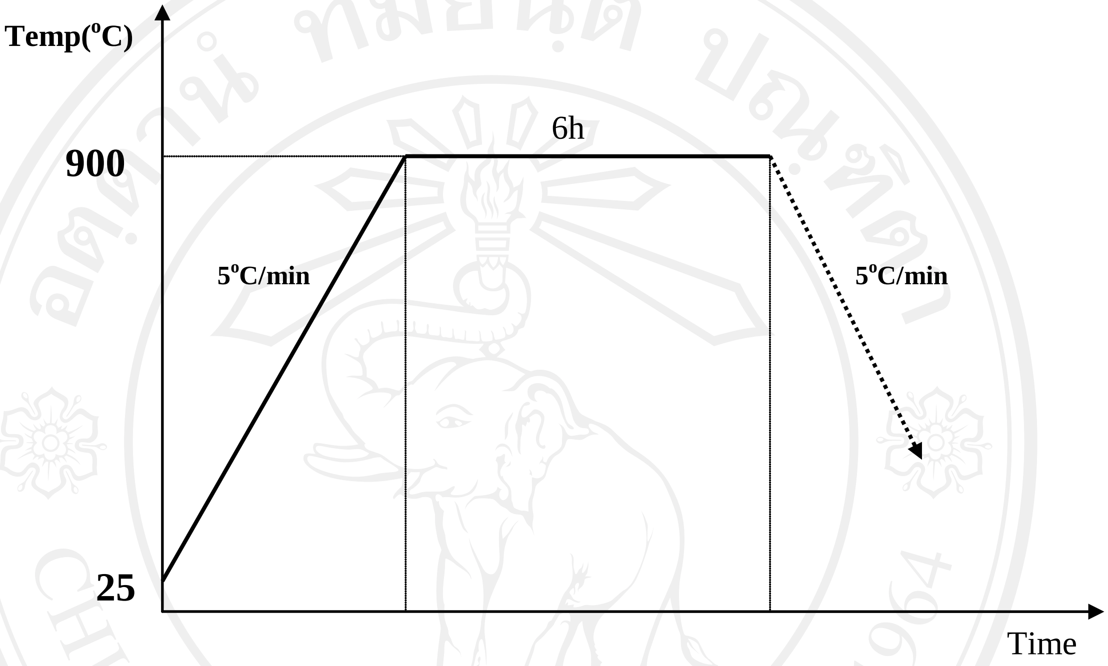

Figure 3.2 Schematic diagram of the calcination schedule for $CaCu_3Ti_4O_{12}$ powder

3.1.4. Pressing of the $CaCu_3Ti_4O_{12}$ samples

It is necessary to provide the binding force among the calcined particles in order to make a green ceramic pellet of $CaCu_3Ti_4O_{12}$. With the dried powder, approximately 3 wt% of polyvinylalcohol or PVA was mixed together in the mortar. Then weight of the $CaCu_3Ti4O_{12}$ powder (0.8 gram) for making a single pellet was measured via a digital balance. The powder was inserted into the central hole (diameter = 12 mm) of a cylindrical mould where a small cylindrical spacer was

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already put in the bottom. After closing the top of the hole by putting another cylindrical spacer, which is longer than the one in the bottom, the entire mould was put into the stage of a cold uniaxial press (Carver Press, Inc.), shown in Figure 3.3. The $CaCu_3Ti_4O_{12}$ powder was pressed up to 1500 psi for 3 minutes to produce a green ceramic pellet.

Figure 3.3 Photo image of a cold uniaxial press (Carver Press, Inc.)

3.1.5. Firing process of the $CaCu_3Ti_4O_{12}$ samples

After the process of producing ceramic pellets of $CaCu_3Ti_4O_{12}$ via cold press, these green products require a certain amount of bonding among the particles to obtain the desired properties and microstructures. As a traditional method, heat treatment has been used for this purpose by heating up these green ceramics to a certain temperature where no phase transition occurs. This process is called firing and it has three steps: 1) pre-sintering

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2) solid-state sintering

3) cooling [51].

Based on these stepwise processes, the complete firing schedule of $CaCu_3Ti_4O_{12}$ samples is shown in Figure 3.4. Since the green samples include the organic additive that must be completely removed to avoid the undesirable effects on the properties of the final products, slow heating rate (3 °C/min) is required until temperature reaches 500 °C around which the most amount of PVA decomposes. After 2 hours of holding at that temperature to complete the organic burnout, $CaCu_3Ti_4O_{12}$ samples were then heated up to 1100 °C in air with the rate of 5 °C/min for the solid state sintering process. After 4 hours of holding, the $CaCu_3Ti_4O_{12}$ samples were cooled down to room temperature with the control of cooling rate (5 °C/min). For the study of the effects of different processing conditions.

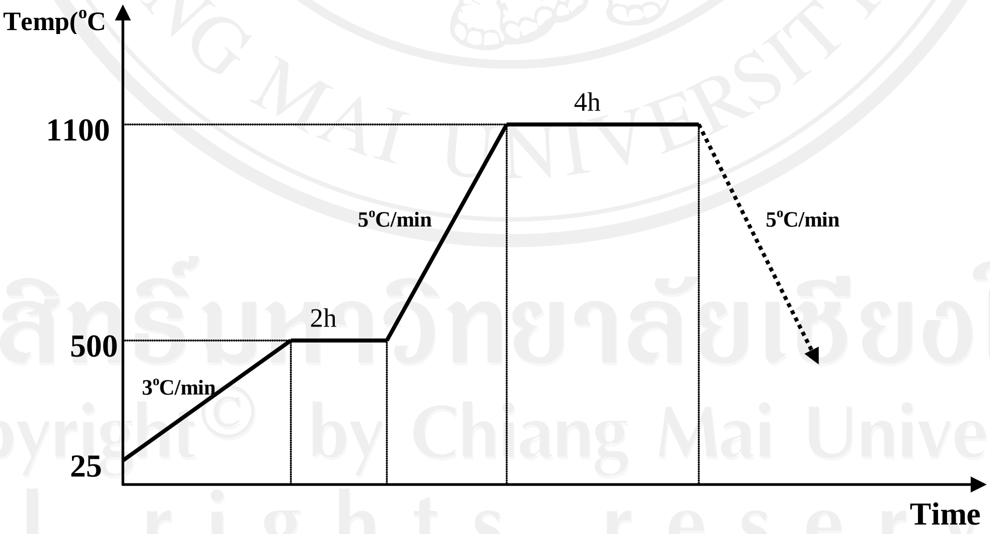

Figure 3.4 Schematic diagram of sintering schedule for the calcined $CaCu_3Ti_4O_{12}$ powder

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Figure 3.5 Photo image of a electric furnaces (Protherm furnances)

3.2. Measurement techniques

3.2.1. Sample preparation prior to the measurements

3.2.1.1. Structure Determination

To determine the phase purity and lattice parameters of calcined powder and ceramics samples, the x-ray diffraction technique was performed by x-ray diffractometer (Bruker-AXS D8) in the 2θ scan range of 10°-70°, shown in Figure 3.6. The source of X-ray employed Cu-Kα radiation, with a tube voltage and current of 40 kV and 40 mA, respectively. Room temperature XRD data was collected with step size of 0.02 at a scanning rate of 10^o per minute. The peaks of x-ray diffraction pattern were determined and analyzed by EVA software. The lattice parameter calculation was based on least square method according to each peak.

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Figure 3.6 Photo image of a x-ray diffractometer (Bruker-AXS D8)

3.2.1.2. Density Measurement

The densities of ceramics were obtained using the Archimedes method which was described in the following equation [56]:

$$\rho = \frac{w_d}{w_0 - w_i} \tag{3.1}$$

Where W_d is dry weight and W_i is sample weight in the water. W_0 is the weight of sample after take out from water.

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3.2.1.3. Sample Preparation

Prior to making dielectric measurements, the samples were polished to obtain smooth and parallel surfaces. In order to avoid the fringing filed effects, thickness of the samples were polished down to the size of 1mm which makes the thickness less than 1/10 of diameter. The silver electrodes were applied to samples according the measurement type and temperature range. For dielectric properties as a function of temperature, after polishing, a silver electrode paste (Heraeus C1000) was applied on the surface and then fired at 750°C for 20 mins with heating rate of 2^{o}C per min.

3.3. Measurement of electrical properties

3.3.1 Dielectric Properties Measurement

The dielectric measurements were consisted of an LCR meter (Agilent 4284A, Hewlett-Packard Inc.), measurement unit and a desktop computer which was operated by Labview program (National Instrument). For low temperature dielectric measurement, this system was combined with environmental chamber (model 9023 delta design Inc.) which was capable of making dielectric measurements in the frequency range of 100 Hz to 100 kHz and temperature range of roomtemperature to 150^{o}C. When higher temperature measurements were required, a high temperature measurement cell (NorECS Probostat) was used. This instrument was designed to work from room temperature to 1600oC. The heating rate during measurement is ± 2^{o}C/min in air, while the capacitance and loss were measured using an applied ac voltage of 1 V at frequencies between 100 Hz to 100 kHz. The dielectric constant (ε_r) was calculated by the following Eq. 3.2:

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$$\varepsilon_r = \frac{Ct}{\varepsilon_o A} \tag{3.2}$$

Where C is the capacitance (Farad), ε_r is the permittivity of free space (8.854 x 10^{-12} F/m), and A and t are the electrode area and thickness of the sample in meters, respectively

3.3.2. Capacitance measurement

The measurements of capacitance versus voltage of both stoichiometric and doped $CaCu_3Ti_4O_{12}$ pellets were carried out via LCR meter. With the help of TRS Technologies Inc., capacitance measurements at high voltages were performed (up to 500 V) using the bipolar sweep mode with four-second delay. Also, the current-voltage (I-V) measurements were carried out by a Keithley 237 source-measure unit with the applied bias up to 50 V in order to calculate the resistivity of $CaCu_3Ti_4O_{12}$ pellets. On the other hand, both grain resistivity and boundary resistance of $CaCu_3Ti_4O_{12}$ pellets were measured by using an impedance analyzer (Model 4194A, Hewlett-Packard) over the frequency range of 10 Hz – 5 MHz. All impedance data were collected through a LabVIEW® software and analyzed via Microsoft Excel® and Kaleidagraph® spreadsheets. The measurement equipments and their setup are shown in Figure 3.7.

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Figure 3.7 Photo images of the dielectric (Agilent 4284A LCR meter) and electrical measurement system (HP 4194A impedance analyzer)

3.3.3. Resistivity Measurements

The resistivity is obtained by the technique of complex impedance spectroscopy (CIS). CIS is a powerful technique, which is used to investigate the electrical processes occurring in a material on applying AC input signal. The complex impedance can be written as Eq.3.3. :

$$Z(\omega) = Z'(\omega) + iZ''(\omega) \tag{3.3}$$

Where Z' represents the resistance, Z" is the reactance and ω is the measurement frequency ($\omega = 2\pi f$). According to the Debye model the frequency dependence of the impedance can be written as following Eq.3.4.

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$$Z'(\omega) = R_g + \frac{R_{gb} - R_g}{1 + \omega^2\tau^2} \qquad (3.4)$$

Where R1 and R2 are the high and low frequency resistances, respectively. The relation between resistance and reactance can be expressed in terms of relaxtion time (τ) and is shown in Figure 3.8.

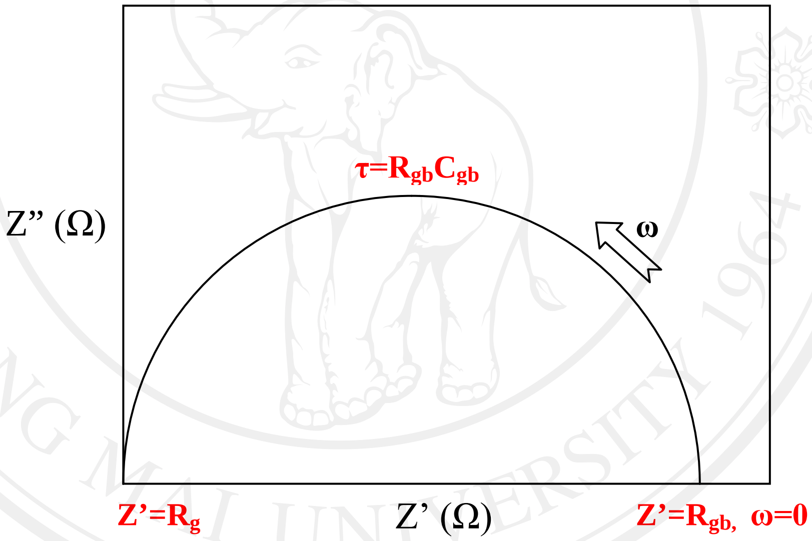

Figure 3.8 Complex impedance plot

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