

## Chapter 3

### Experimental procedure

The experimental conditions, techniques of sample preparation and the measurements of physical and thermal properties as well as microstructure investigation are described in this chapter.

#### 3.1 Raw materials and characterization

##### 3.1.1 Starting raw materials

Oxide and nitrate as listed in Table 3.1 were used as starting raw materials. The composition data for each material was received from the suppliers.

Table. 3.1 Oxide powders and chemicals used in this experiment.

Materials	Purity	Average particle size( $\mu\text{m}$ )	Manufacturers
Aluminium oxide AKP-30	>99.99%	0.3	Sumitomo
Aluminium oxide AES-11	99.8%	0.5	Sumitomo
Magnesium(II) nitrate $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	$\geq 99\%$	-	Fluka
Zirconium oxide TZ- 3Y	3 mol% $\text{Y}_2\text{O}_3$	-	TOSOH

Aluminum oxide, AKP-30 and AES-11, were used as raw materials considering their purity and particle size as shown in Table 3.1 and their cost. A price of AKP-30 is about 2,000 baht/Kg and AES-11 is about 250 baht/Kg. AKP-30 is high purity with fine  $\alpha$ -alumina powder that composed of uniform crystal size, with of sharp particle size distribution. AKP-30 is suited for translucent alumina ceramics. AES-11 is a medium grade with fine and uniform  $\alpha$ -crystal size. AES-11 also has good sinterability and high molding density, which makes the reduction of the linear shrinkage possible.

### 3.1.2 Raw material characterization

#### 3.1.2.1 Particle size distribution determination

Particle sizes distribution of AKP-30 and AES-11 were measured using sedimentation method with centrifugal particle size analyzer (Shimadzu SA-CP2). About 1 gram of alumina powder was mixed with 0.2wt% NaHMP solution before subjected into the centrifugal particle size analyzer. A solution with 0.2wt% NaHMP was used as a blank solution.

#### 3.1.2.2 Microstructure examination by scanning electron microscope (SEM)

Morphology of AKP-30 and AES-11 was examined using a scanning electron microscope (JEOL : JSM-1670). Alumina powders were dispersed in distilled water using ultrasonic for 5 min. The alumina solution was dropped on a glass slice, dried and then gold sputtered before subjected into the microscope.

### 3.2 Composition and preparation of alumina powder

All compositions which are shown in Table 3.2, were prepared by conventional oxide mixing process. The flow chart of preparation is illustrated in Fig.3.1. The raw materials were added with various additives, MgO and ZrO<sub>2</sub>. Both additives prevent discontinuous grain growth and allow the material to be sintered to theoretical or nearly theoretical density. The amount of MgO was selected at 0.5 wt% based on the data shown in Fig.2.3. The amounts of ZrO<sub>2</sub> were selected at 1.5, 3 and 7.5 wt%. 100 gram of raw powders were wet mixed in polypropylene bottle (250 ml) for 4 hours, using alumina balls as grinding media and 150 ml of distilled water as solvent. Alumina balls were filled to a half volume of the bottle. The mixture was filtrated and dried at 105 °C overnight in an oven to remove the solvent. Before forming, the mixture was well mixed with 1.0 wt% of polyvinyl alcohol (PVA with 9000 - 10000 MW) acted as a binder and was sieved through a 100 mesh screen. Twenty gram of the polyvinyl alcohol was dissolved to 100 ml of water. The specimen was pressed into pellets of 12, 25 and 35mm in diameter by biaxial hydraulic press with 20 MPa pressure. All specimens were heated to 540 °C for 2 hours with heating rate of 5 °C/min for binder removal. Further raised the temperature at a heating rate 5 °C/min to 1450, 1500, 1550, 1600 and 1650 °C with a soaking period of 1, 2, 4 and 6 hours for densification. The sintered samples were cooled to 35 °C in the furnace.

Table.3.2 Compositions of Alumina for Peltier element

Sample.	Alumina	Additives (wt%)	
		MgO	ZrO <sub>2</sub>
2-1.	AKP-30	-	-
2-2.	AKP-30	0.5	-
2-3.	AKP-30	-	1.5
2-4.	AKP-30	-	3.0
2-5.	AKP-30	-	7.5
2-6.	AES-11	-	-
2-7.	AES-11	0.5	-
2-8.	AES-11	-	1.5
2-9.	AES-11	-	3.0
2-10.	AES-11	-	7.5
1-1.	AKP-30	0.5	1.5
1-2.	AKP-30	0.5	3.0
1-3.	AKP-30	0.5	7.5
1-4.	AES-11	0.5	1.5
1-5.	AES-11	0.5	3.0
1-6.	AES-11	0.5	7.5

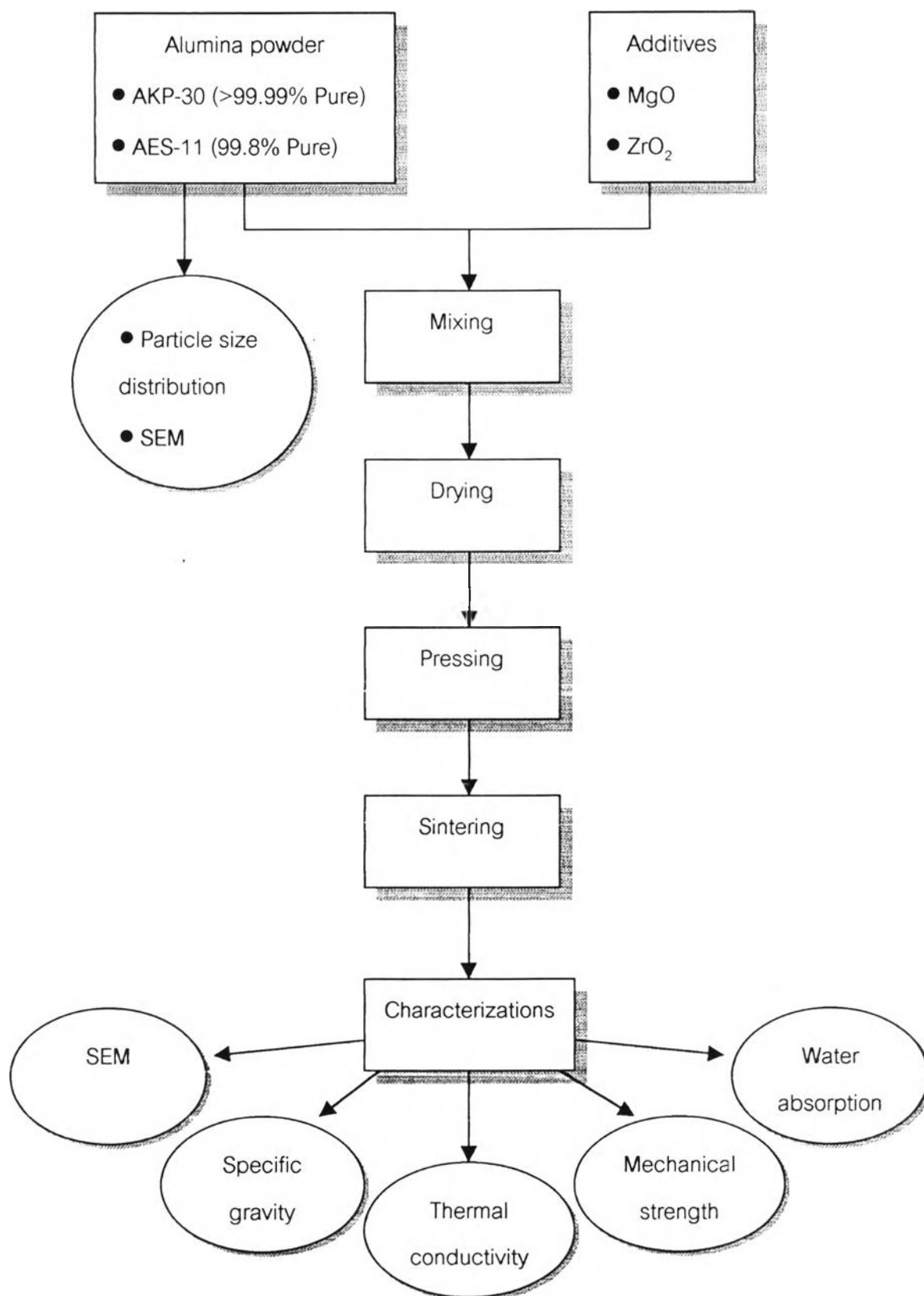


Fig. 3.1 Flow diagram of sample preparation of Peltier element by a conventional oxide mixing process.

### 3.3 Characterization of sintered specimens

#### 3.3.1 Density measurement

##### 3.3.1.1 Bulk density

The bulk density of specimens was measured according to Archimedes method. The air in opened pores of specimen were removed by vacuum pressure for 30 min and then pour water onto specimens until all specimens submerged in water. Water was removed to the opened pores by vacuum pressure for 1 hr. The dry weight  $W_d$ , Saturated weight  $W_{sat}$  and Suspended weight  $W_{sus}$  were measured and used to calculate the bulk density using equation (3.1) following ASTM standard (Designation : C830-93)

$$\text{Bulk density} = \frac{W_d}{W_{sat} - W_{sus}} \rho \quad (3.1)$$

Where  $\rho$  is water density at the measurement temperature (0.99568 g/cm<sup>3</sup> at 30 °C).

##### 3.3.1.2 Theoretical density

The theoretical density of sintered Peltier elements pellets were calculated from real density using the following equation.

$$\text{Theoretical density} = \frac{W_{total}}{W_a/\rho_a + W_b/\rho_b + \dots} \quad (3.2)$$

Where  $W_{total}$  is total weight of used components.

$W_a, W_b$  is weight of component a and b, respectively.

$\rho_a, \rho_b$  is real density of component a and b, respectively.

a, b, ... is used component.

In this experiment, used as the theoretical density of pure  $\text{Al}_2\text{O}_3 = 3.97 \text{ g/cm}^3$ ,  $\text{MgO} = 3.64 \text{ g/cm}^3$  and  $\text{ZrO}_2 = 6.023 \text{ g/cm}^3$  were used for calculate. As a result theoretical density of compositions are calculated and shown in Table 3.3.

Table 3.3 Calculated 100% density of each composition.

Composition	Calculated 100% density ( $\text{cm}^3$ )
2.1, 2.6	3.97
2.2, 2.7	3.97
2.3, 2.8	3.99
2.4, 2.9	4.01
2.5, 2.10	4.07
1.1, 1.4	3.99
1.2, 1.5	4.01
1.3, 1.6	4.07

### 3.3.1.3 Relative density

The relative density calculated from bulk density and theoretical density using the following equation.

$$\text{Relative density} = \frac{\text{Bulk density}}{\text{Theoretical density}} \quad (3.3)$$

### 3.3.2 Water absorption measurement

Water absorption of specimens were measured according to Archimedes method using equation (3.3)

$$\text{Water absorption (\%)} = \frac{W_{\text{sat}} - W_{\text{d}}}{W_{\text{d}}} \cdot 100 \quad (3.4)$$

Where  $W_{\text{sat}}$  is saturated weight and  $W_{\text{d}}$  is dry weight of the specimens.

### 3.3.3 Microstructure examination by scanning electron microscope (SEM)

Microstructure of specimens sintered at 1600°C and 1650 °C were examined using a scanning electron microscope (SEM) (JEOL : JSM-1670). The as sintered specimens were polished with various size of diamond paste and finished with 1 μm diamond paste using Buehler machine with 10 pound load and 200 rpm at each size of diamond. And then thermally etched at 1500 °C for 30 min. The specimens were gold sputtered before subjected into the microscope. The average grain size were determined by a line intercepted method following ASTM standard (Designation E 112-96)

### 3.3.4 Strength measurement

The compositions No. 2-6, 2-7, 2-8, 2-9, 2-10 in Table 3.2 were pressed into the pellets of 35 mm diameter by hydraulic press with 20 MPa pressure. All specimens were sintered at 1450, 1500, 1550, 1600 and 1650 °C for 2 hours. The surface of sintered samples were ground with 200 mesh diamond wheel using grinding machine at MTEC for parallel surface and then polished using SiC paper Grit number 240 (Buehler grinding paper). All specimens were annealed at 1500 °C for 30 min except the specimens that were sintered at 1450 °C. The test specimen was placed on three symmetrically spaced points near its periphery as shown in Fig.3.2 and Appendix 3. It is bent in a cupping fashion by the application of force to the center of specimen through a cylindrical ram. Scotch tape was attached to the compression side of each specimens to prevent the scatter of specimen after break. The force is applied to the ram at the rate of 25 mm/min in compression test machine (LLOYD Instrument LTD) with load cell 100 KN. The breaking load, the dimensions and elastic constants of the specimen, and the radii of the support and load are used for calculate the maximum tensile stress which is at the center of the tension surface following the ASTM standard (Designation F 394-78)

$$S = -0.2387P(X-Y) / d^2 \quad (3.5)$$



Where  $S$  = maximum center tensile stress (MPa),

$P$  = total load causing fracture (N),

$X = (1+\nu) \ln(B/C)^2 + [(1-\nu)/2](B/C)^2$ ,

$Y = (1+\nu)[1 + \ln(A/C)^2] + (1-\nu)(A/C)^2$ ,

$\mu$  = Poisson's ratio, 0.23,

$A$  = radius of support circle (mm),

$B$  = radius of loaded area or ram tip (mm),

$C$  = radius of specimen (mm), and

$d$  = specimen thickness at fracture origin (mm)

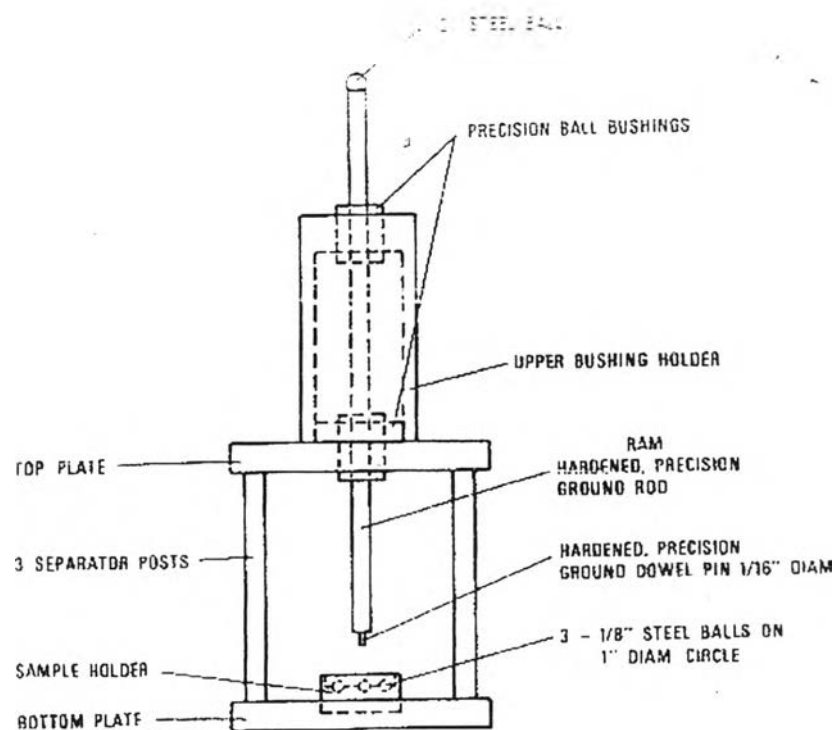


Fig.3.2 Biaxial-flexure strength –test fixure in ASTM F 394-78.

In this experiment ;

$A = 12.5$  mm

$B = 0.25$  mm, it was measured from the contact area using optical microscope.

$C = 12-15$  mm, exact value is shown in Appendix9.

$d = 2.3-2.7$  mm, exact value is also shown in Appendix 9.

### 3.3.5 Thermal conductivity measurement

The mixtures were pressed into the pellets of 12 mm diameter by hydraulic press with 20 MPa pressure. Specimens were sintered at 1600 °C and 1650 °C for 2 hours with 5 °C/min heating rate. The surface of sintered samples was ground using various grinding SiC paper 250, 400, 800, and 1200 mesh and 30 pound load for 30 min each. Then polished with diamond paste using 6 μm, 3 μm and 1 μm diamond pastes with 10 pound load for 15 min.

The thermal conductivity of specimens were sent to measured by Laser Flash method at ULVAC – RIKO, Inc. Japan. The test specimen was mounted horizontally or vertically is subjected to a high-intensity short duration thermal pulse. The energy of the pulse is absorbed on the front surface of a specimen and resulting rear face temperature rise is measured. The ambient temperature of the specimen is controlled by a furnace or cryostat. Thermal diffusivity values are calculated from the specimen thickness and the time required for the rear face temperature rise to reach certain percentages of its maximum value following the ASTM standard (Designation : E 1461-92). The essential features of the apparatus are shown in Fig.3.2. These are the flash source, sample holder and environmental system, temperature response detector, and data collection and analysis components.

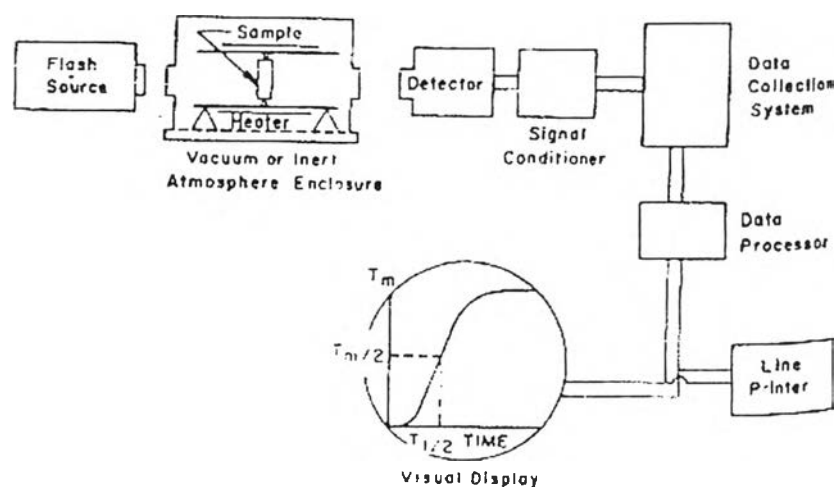


Fig.3.2 Flash diffusivity apparatus (Schematic).