CHAPTER III

EXPERIMENTAL PROCEDURES

3.1 Characterization of raw materials

The different characteristics of raw materials have been affected to final properties of glass-ceramic materials. Therefore, the compositions and properties of starting materials should have been characterized.

3.1.1 Zinc hydrometallurgy waste

Type of zinc minerals and materials adding during zinc recovery process have been affected to compositions of Zn-waste, thus, compositions and other properties of Zn-waste used in this study were characterized by using various techniques as follows:

- Visual observation was taken by a digital camera (μ[mju:] 300 digital, Olympus Optical Co., Ltd. Japan)

- The chemical compositions were determined by X-ray fluorescence analyzer (XRF; Phillips PW-2400)

- Particle size distribution was analyzed by using Master sizer (Malvern, Mastersizer S Ver.2.19, UK) with water as a medium.

- Thermal analysis was performed by a differential thermal analysis (DTA; Perkin Elmer, DTA7, USA). The temperature condition was set from 30°C to 1100°C with a heating rate of 10°C/min in air.

- Crystalline phases were characterized by X-ray diffractrometer (XRD; Bruker D8 Advance, Germany) with CuK_{α} radiation, $10^{\circ}<2\theta<70^{\circ}$, scan speed of 0.02°/sec, 40 KV and 40 mA.

3.1.2 Glass cullet

The two types of glass cullet employed in this study were clear cullet, from float glass industry and amber cullet, from container glass industry. Chemical compositions of two different types of cullet were investigated by X-ray fluorescence analyzer (XRF; Phillips PW-2400).

3.2 Characterization of glass-ceramics obtained by non-melting process

The conventional method for producing glass-ceramics was required to melt raw materials at first to achieve the parent glasses following by devitrify the glass by a two-stage heat treatments [4]. There are several problems such as economical loss from thermal process. For this reason, reduction steps in fabrication process of glass-ceramics have been attended in this research.

Zn-waste and clear cullet were ground in order to get powder through a sieve 100 mesh (~150 μm). The waste powders were mixed together in the proportion Zn-waste from 10-90% by weight. Moreover, influence of different particle size of the formers on physical properties was included in this study. Thus, the mixtures of each batch were dry ground by ball mill for 20 minutes in a high speed porcelain ball mill to get particle size finer than 44 μm (-325 mesh). The powders of each composition (both coarse and fine powder) were pressed into a pallet shape (2 mm in diameter and 0.5 mm in thickness) by an uniaxial compression under a pressure of 100 MPa without binder. Green specimens were placed in an electrical furnace and heated to 800°C for 1 hour to removal the volatile materials, followed by heating to various temperature (1000, 1050, and 1100°C) and held for 2 hours for crystal growth using a heating rate of 5°C/min. After heat-treatment, volume shrinkage and physical properties of fired specimens, i.e. apparent porosity, water absorption, apparent density, and bulk density were determined by using Archimedes' method. Strength of samples was tested by three-point bending method from samples of dimensions 10×60×5 mm^3, 5 pieces, using universal testing machine (LLOYD500, Intro enterprise Co., Ltd.) with a 45 mm span length at a crosshead speed of 0.5 mm/min. Porosity of specimens was also observed

by optical microscope (OM; Olympus BX60M, Olympus optical Co., Ltd., Japan). The flowchart of this process was showed in Fig. 3.1.

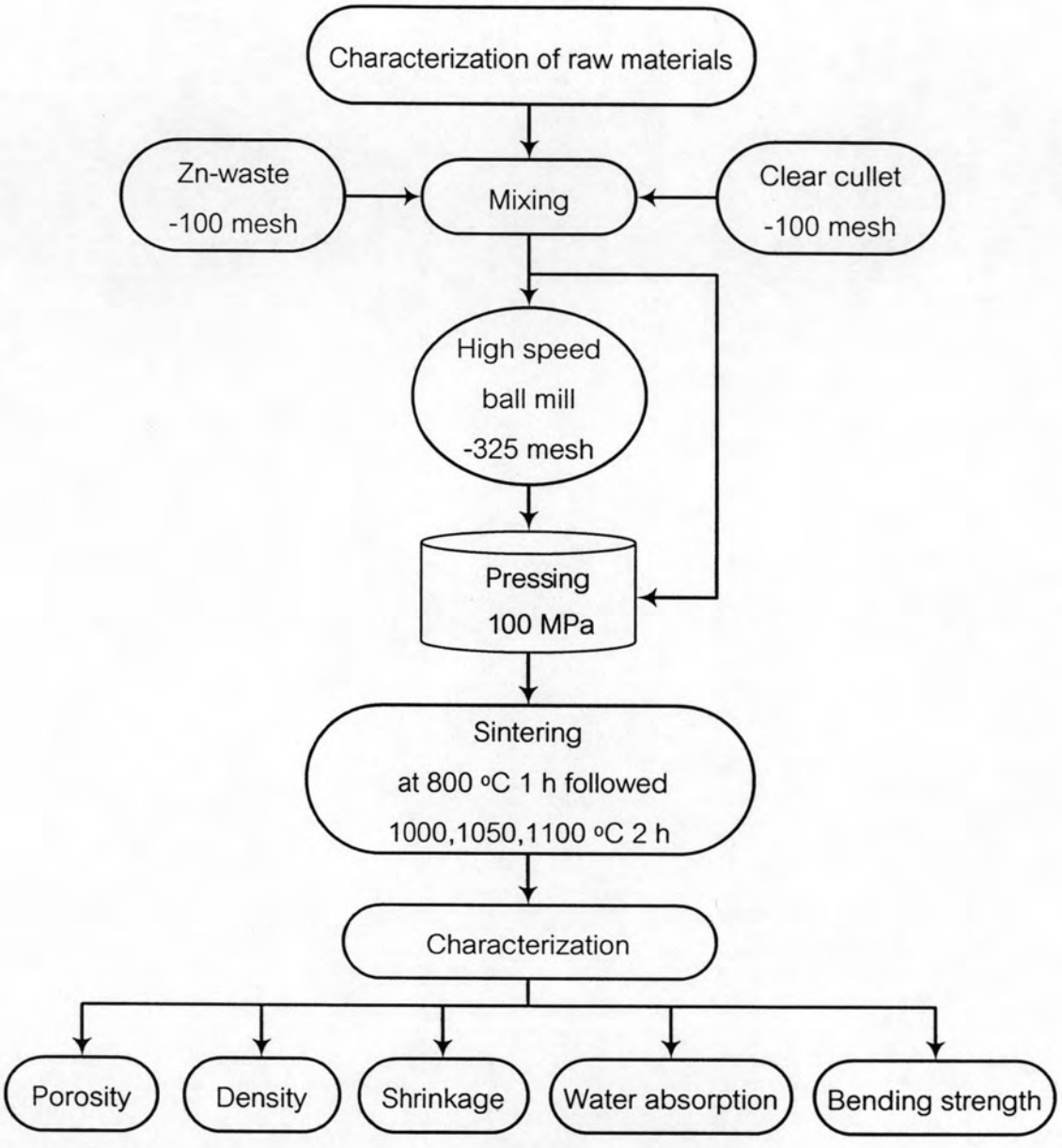

Fig. 3.1 Preparation of glass-ceramics by non-melting process

3.3 Glass-ceramics obtained by melting and sintering process.

3.3.1 Glass Preparation

Raw materials used in this process were Zn-waste, clear cullet, and amber cullet. For ease in the melting process, the raw materials were crushed to obtain fine powder. Mixtures of 0, 20, 40, 60, and 100 wt% Zn-waste with clear cullet and amber cullet in the same proportion were melted in an electrical furnace (Heraeus, Germany) in alumina-zircon crucible at 1450°C for 1 hour to ensure homogenous melting and then poured onto a preheated steel plate to prevent thermal shock after cooling down to room temperature. Parent glasses of each batch composition were obtained.

3.3.2 Characterization of parent glasses

3.3.2.1 Physical properties

- Visual observation was observed homogeneity and color of parent glasses.

- Bulk density was determined by Archimedes' method.

3.3.2.2 Thermal behavior

To determine the crystallization temperature of glass powders, differential thermal analysis (DTA; Perkin Elmer, DTA7, USA) was used to investigate glass transition temperature, T_g and crystallization temperature, T_c of the glasses. Twenty milligrams of glass powder and standard alumina powder (reference material) were loaded in platinum crucibles then heated from 100°C to 1200°C with a heating rate of 10°C/min. Crystallization temperature was selected as sintering temperature in this study.

3.3.2.3 Thermal expansion coefficient

- Thermal expansion coefficient of parent glasses was investigated using dilatometer (NETZSCH DIL 402C, USA) in the range of 35-350°C.

3.3.3 Glass-ceramics preparation

Parent glass was ground to set fine powder through a sieve 100 mesh (~150 μm) then it was pressed into a bar shape (10×60×5 mm^3, 5 pieces) with pressure 100 MPa and used 5 wt% of polyvinyl alcohol (PVA) solution as a binder (1 wt% of PVA solid in water). After drying at 110°C for 24 hours in an oven, pressed specimens were sintered in a furnace (MAXTERMO MC-2838, Interkilns industry Co., Ltd.) at 750°C and 850°C for 2 hours with a heating rate of 10°C/min for crystallization process and transformed to glass ceramics. After cooling, glass-ceramics were cleaned by water and dried in the oven at 100°C for 24 hours.

3.3.4 Characterizations of glass ceramics

3.3.4.1 Physical properties

a) Visual observation

Physical character, i.e. such as shape, surface, and color of fried specimens were investigated. Photographs were taken by a digital camera (μ[mju:] 300 digital, Olympus optical Co., Ltd., Japan).

b) Shrinkage

Linear shrinkage of glass-ceramic specimens was calculated as follows:

$$\% \text{ Linear shrinkage} = \left[\frac{(l_1 - l_2)}{l_1}\right] \times 100 \qquad \text{(eq. 3.1)}$$

Where; l_1 is length of specimen before firing

l_2 is length of specimen after firing

Volume shrinkage of glass-ceramic specimens was calculated as follows:

$$\% \text{ Volume shrinkage} = \left[\frac{(V_1 - V_2)}{V_1}\right] \times 100 \qquad \text{(eq. 3.2)}$$

Where; V_1 is volume of specimen before firing

V_2 is volume of specimen after firing

c) Apparent porosity, water absorption, and bulk density

Apparent porosity ($A.P$), water absorption ($W.A$), and bulk density ($B.D$) of glass-ceramics were determined by Archimedes' method following ASTM C373-88 [21]. The equations for calculation are shown as follows:

$$W.A. = \left[\frac{(W_3 - W_1)}{W_1}\right] \times 100 \quad \text{(eq. 3.3)}$$

$$A.P. = \left[\frac{(W_3 - W_1)}{(W_3 - W_2)}\right] \times 100 \quad \text{(eq. 3.4)}$$

$$B.D. = \left[\frac{W_1}{(W_3 - W_2)}\right] \times \text{Density of water} \quad \text{(eq. 3.5)}$$

Where, W_1 is dry specimen weight (g)

W_2 is specimen weight in water (g)

W_3 is water filled specimen weight (g)

3.3.4.2 Phase formation

Crystalline phases formed during heat treatment were analyzed using X-ray diffractometer (XRD; Bruker D8 Advance, Germany). Glass-ceramics were ground and loaded in the holder and placed on the stage. A copper X-ray (CuK_{α}) generated at 40 KV and 40 mA was used, in the range of $10^{\circ}<2\theta<70^{\circ}$ with a scan speed of 0.02 °/sec. The crystalline phases of each sample were identified from XRD pattern using computer software (Diffracplus EVA version 7).

3.3.4.3 Microstructure

The crystal morphology and porosity were observed by optical microscope (OM; Olympus BX60M, Olympus optical Co., Ltd., Japan), in addition, scanning electron microscope (SEM; JEOL JSM-6400 model, Japan) was used to substantiate crystal morphology and element compositions of crystals and glass matrix formed in glass-ceramics were characterized by energy dispersive spectrometry; EDS (OXFORD Instrument ISIS 300). Each sample was cut with a diamond wafering blade by the cutting machine in crossed-section, and then mounted in resin, polished using grinder-polisher (BUCHLER METASERV, England) and SiC grinding paper started from #120, #400, #800, and #1200. The mirror-like surface was obtained by polished with diamond paste 1 μm. Polished specimens were cleaned by ultrasonic cleaner (CREST, USA) for 5 minutes in water. Cleaned specimens were etched with 2% hydrofluoric acid (HF) for 10 seconds at room temperature and washed by water immediately and wiped them up with ethanol. Porosity of the specimens was observed by optical microscope before etching. For SEM study, the samples were sputtered with gold for simultaneous microanalysis.

3.3.4.4 Mechanical properties

a) Bending strength

The mechanical strength of glass-ceramics was determined according to ASTM C1161-02C [22] by three point bending method. Five pieces of each composition were tested using an universal testing machine (LLOYD500, Intro enterprise Co., Ltd.) with a 45 mm span length and a crosshead speed of 0.5 mm/min. The bending strength gained by the average values of 5 samples and equation for evaluation is shown as follows:

$$S = \frac{3PL}{2bd^2} \qquad \text{(eq. 3.6)}$$

Where, S is bending strength (MPa)

P is break force (N)

L is span length (mm)

b is specimen width (mm)

d is specimen thickness (mm)

b) Hardness

Hardness indentation was evaluated following ASTM C1327-99 [23] by a Vickers hardness tester (Zwick 3212) from the sample in cross-section with surfaces polished to 1 μm. A test load of 9.81 Newton (1 kg) is specified on a flat surface and time of the full test load which applied duration of 15 seconds. The mean value from 5 times indentation was reported to be hardness of each composition. The equation for calculation is shown as follows:

$$HV = 0.0018544\frac{P}{d^2} \qquad \text{(eq. 3.7)}$$

Where, HV is Vickers hardness (GPa)

P is load (N)

d^2 is average length of the two diagonals of the indentation (mm)

3.3.4.5 Thermal expansion coefficient

Thermal expansion was investigated by a dilatometer (NETZSCH DIL 402C, USA). A sample size about 5×5×25 mm^3 was achieved by cut using the cutting machine (BUCHLER ISOMET 1000, USA) with a diamond wafering blade (BUCHLER, USA) and followed by polishing with a SiC grinding paper #400 (BUCHLER, Germany) to get a parallel surface. A sample was set in the sample holder subsequently heated from room temperature to 350°C with a heating and cooling rate of 10°C/min. The linear coefficient of thermal expansion was calculated from slope of graph between dL/dL_o% and temperature from 35 to 350°C by computer software (NETZSCH TA).

3.3.4.6 Chemical resistance

Chemical substances used in this study were hydrochloric acid solution, 3% (v/v) and potassium hydroxide solution, 30 g/l according to ASTM C650-97 [39]. Test specimens were immersed in both of solutions for 24 hours, cleaned with acetone and dried in an oven at 110°C. After drying, appearance of the treated and untreated area was visually observed and compared. In addition, the specimens which passed visual test were also tested with effect of pencil lines (HB grade) by means of draw several lines on the surface then removed these pencil lines with a damp cloth. The qualified specimens were specimens that are not attacked with test solutions and the pencil lines can remove from the treated surface.

3.3.4.7 Toxic leaching

Because Zn-waste contained small amount of toxic and hazardous elements, i.e. Pb, As, and Cd, fired specimens need to be tested toxic leaching by toxicity characteristic leaching procedure (TCLP) method 1311 [24] to proof that glass-ceramics produced in this study are stable materials. The test methods described as follows.

Firstly, extraction fluid was determined by means of putting 5 grams of the samples which have sample size less than 9.5 mm into distilled water 96.5 ml. The pH of the solution was measured using a pH meter (pH/Ion/Conductivity Meter M320) after stirring about 5 minutes. If the pH value is less than 5, extraction fluid #1 will be used. In contrast, if the pH value is more than 5, added 3.5 ml of 1N HCl, stirred and heated to 50°C for 10 minutes. Measured the pH again after cooling, use extraction fluid #1, if the pH is less than 5, but if the pH is still more than 5, use extraction fluid #2.

Secondly, the extraction fluid #1 was appropriate for this study and prepared by the addition of 5.7 ml acetic acid (CH_3COOH) and 64.3 ml of 1N NaOH to 500 ml of distilled water and then diluted to a volume of 1 liter. The pH value of this fluid should be about 4.93±0.05.

Thirdly, specimens were mixed with extraction fluid in plastic bottles which the ratio of the solid to liquid was 1:20. After agitation at 30 rpm for 20 hours (displayed in

Fig. 3.2), mixtures were filtered to separate solid from liquid and kept the liquid in glass bottles.

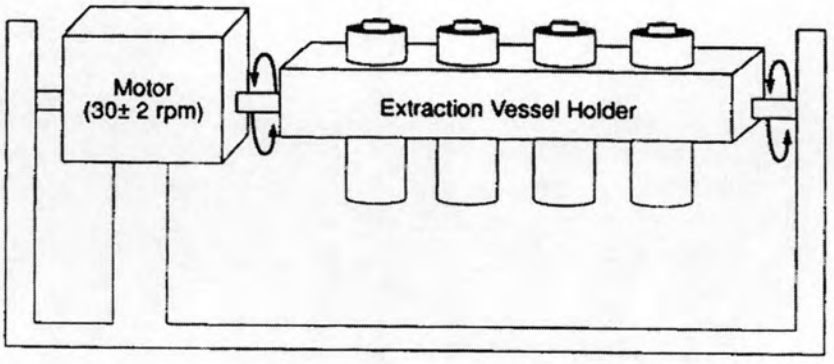

Fig. 3.2 The agitator of toxicity characteristic leaching procedure (TCLP)

Finally, toxic released for lead (Pb) was analyzed from the liquid using atomic absorption spectrometry (AAS, SpectrAA Varian AA280FS), for Arsenic (As) and Cadmium (Cd) were investigated by inductively coupled plasma atomic emission spectrometer (ICP, Perkin Elmer model PLASMA-1000).

Procedure for glass-ceramics preparation obtained by melting and sintering process was shown in Fig. 3.3 and Fig. 3.4.

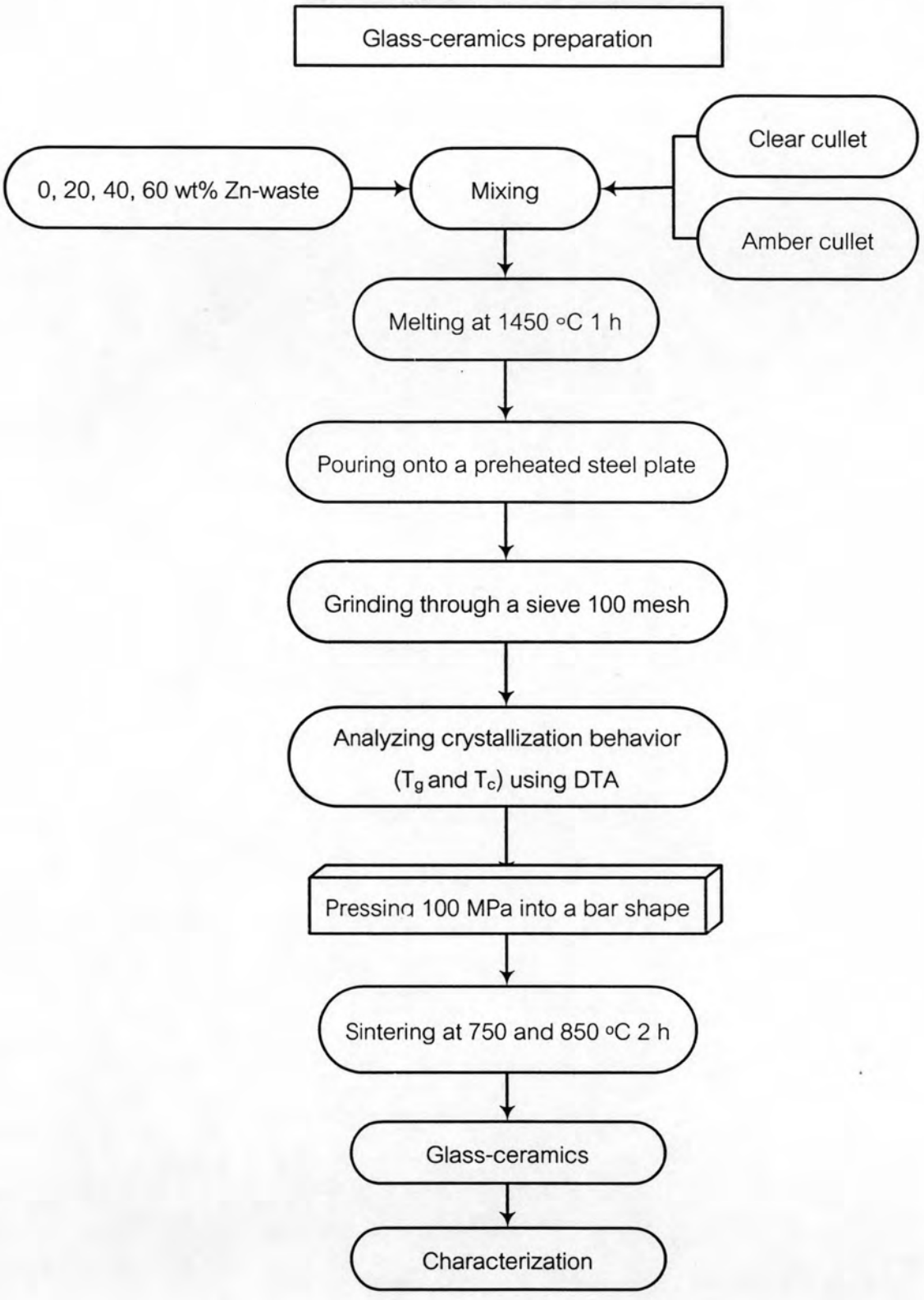

Fig. 3.3 Preparation of glass-ceramics obtained by melting and sintering process

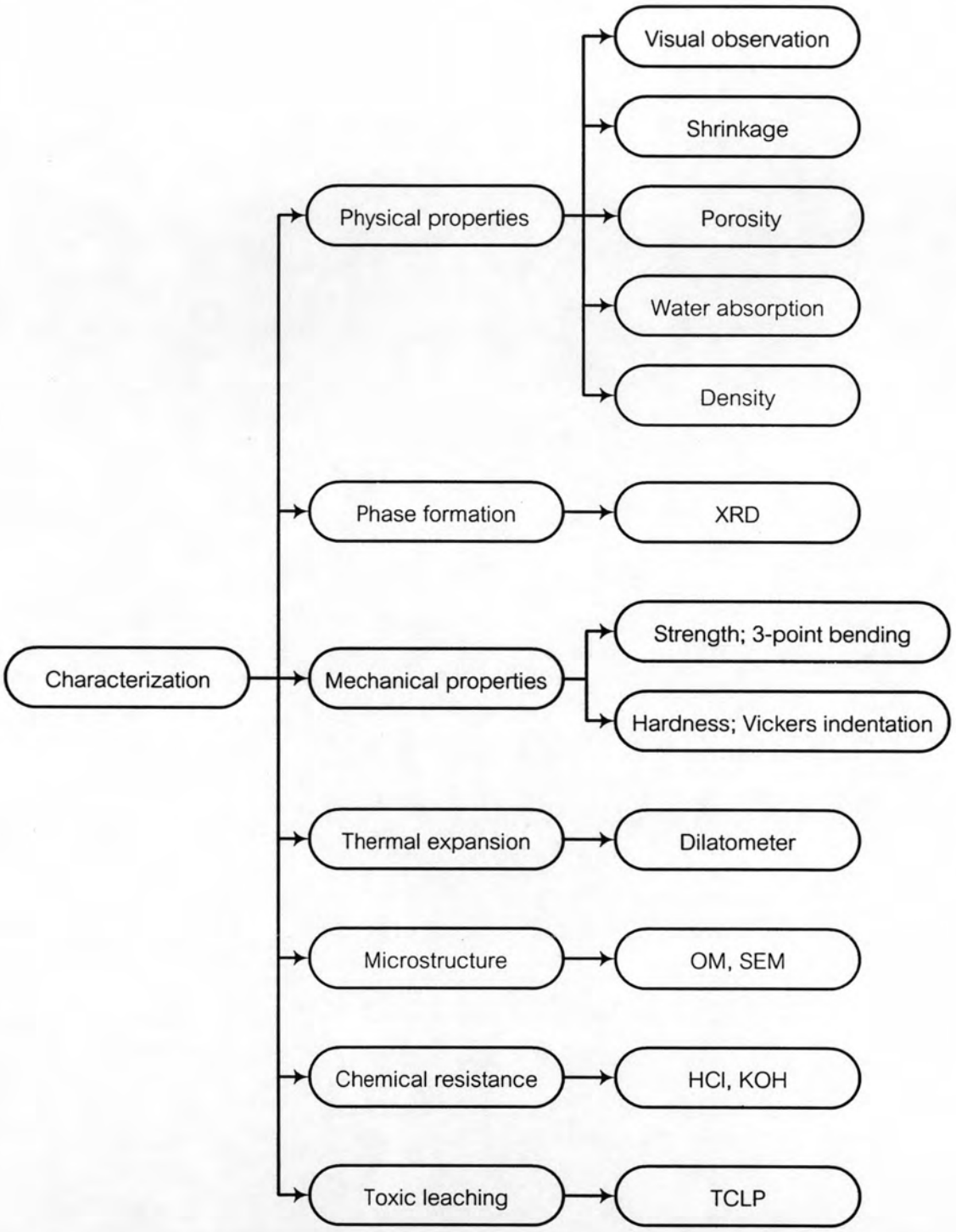

Fig. 3.4 Characterization of glass-ceramics

3.4 Effects of sintering time on physical and mechanical properties of glass-ceramics

As a result of the previous experiment (3.3.4), it was found that a mixture of 60 wt% Zn-waste and 40 wt% clear cullet obtained the highest bending strength. Thus, this composition was to study the influence of sintering time on physical and mechanical properties of glass-ceramics. The procedure of this experiment was illustrated in Fig. 3.5.

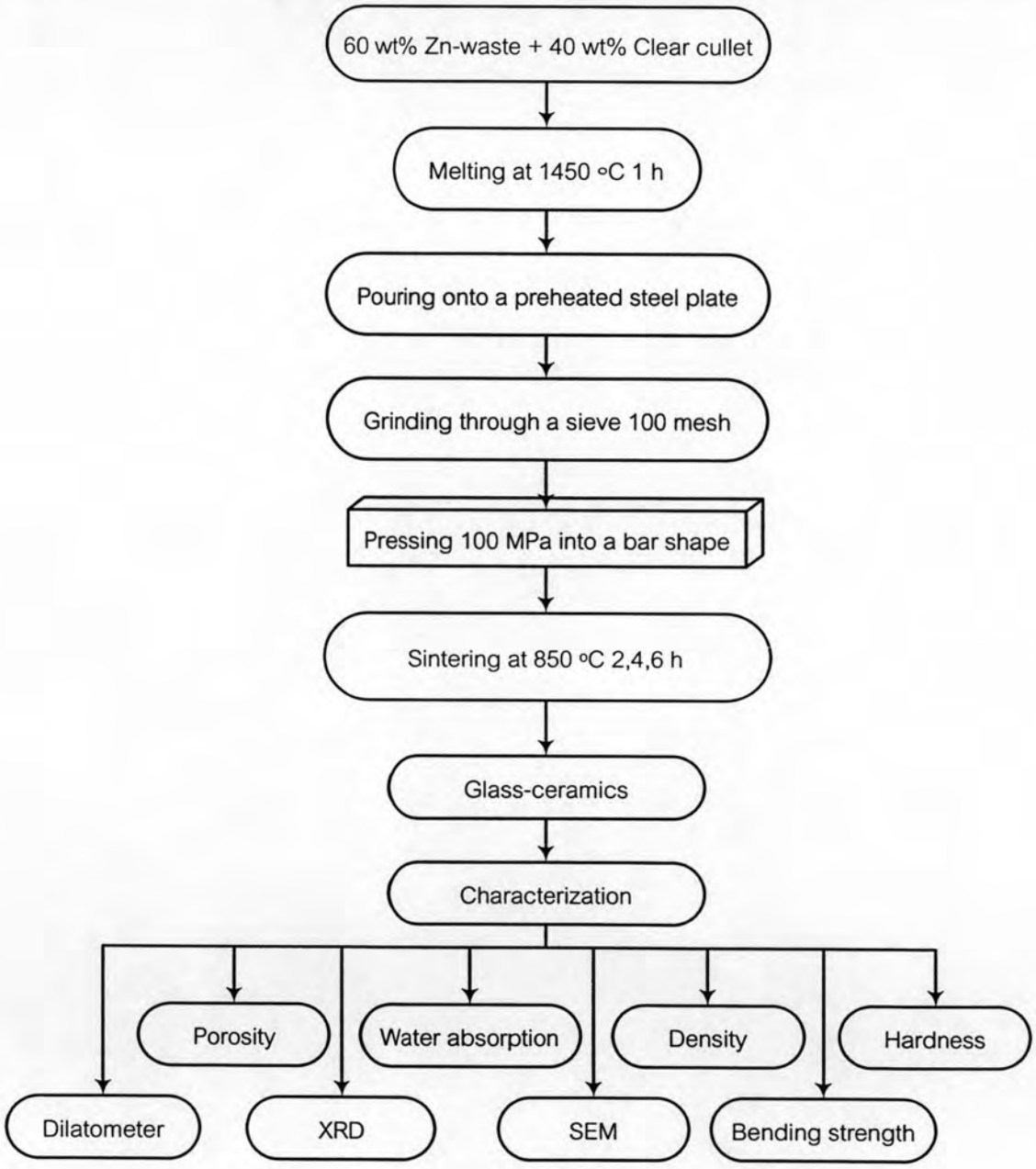

Fig. 3.5 Flowchart of study the effects of sintering time on properties of glass-ceramics

3.5 Application of glass-ceramics as an artificial marble

In order to raise value of zinc hydrometallurgy waste (Zn-waste) and glass cullet, artificial marbles were produced and suitable for wall tiles use. Decorative design of artificial marbles in this study was imitated the natural marbles by using clear cullet as matrix and utilization from different colors of glass powders which depend on varying proportions of Zn-waste. The suitable ratio of clear cullet to glass powder is 6:1. Mixed them together and pressed under a pressure of 100 MPa into a bar shape and used 5 wt% of polyvinyl alcohol (PVA) solution as a binder. Green samples were sintered at 750°C and 850°C in duration of 2 hours and characterized the properties after firing. The series of this experiment was illustrated as flowchart in Fig. 3.6.

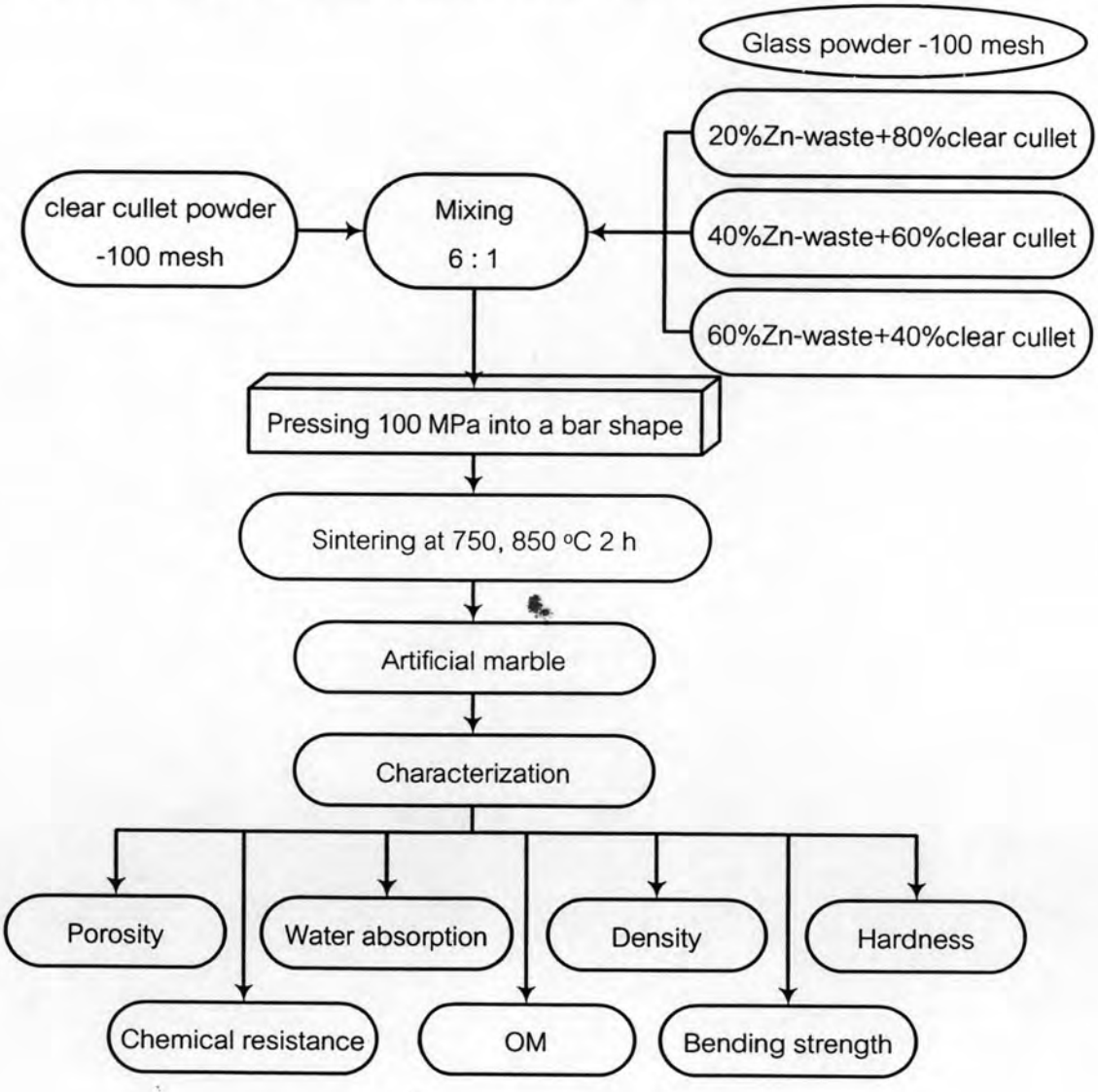

Fig. 3.6 Preparation method of artificial marble