

CHAPTER 3

EXPERIMENT & METHOD

A co-precipitation method similar to that used by Haneda et al. (1974) was used for the preparation of the precursors of the Sn-Co substituted BaF having the nominal composition $BaFe_{12-2x}Sn_xCo_xO_{12}$. Although many methods for the formation of the precursor for BaF have been reported, Haneda et al were the first to prepare BaF using chemical co-precipitation. The reagents used for this method are readily available and are not expensive.

3.1 Materials

The synthesis of the BaF has been performed using the following chemicals:

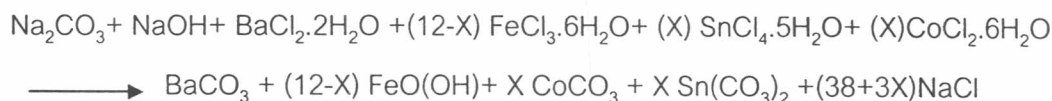
1. BDH barium chloride dihydrate ($BaCl_2 \cdot 2H_2O$, 99% purity)
2. BDH ferric chloride hexahydrate ($FeCl_3 \cdot 6H_2O$, 99% purity)
3. Fluka cobalt chloride hexahydrate ($CoCl_2 \cdot 6H_2O$, 98% purity)
4. Lump Baker Analyzed stannic chloride pentahydrate ($SnCl_4 \cdot 5H_2O$, assay 101.8%)
5. AKZO Nobel sodium hydroxide (NaOH, 98% purity)
6. Fluka (Na_2CO_3 , 99% purity)
7. Lump Baker Analyzed stannic chloride pentahydrate.
8. Doubly distillation water

3.2 Preparation method

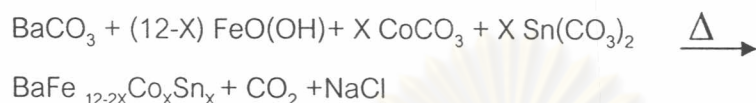
3.2.1 Precursor preparation

The constituents for several mixtures are given in Table 3.1 The mole ratios of Fe:Ba are between 8.1:10.1 while the mole ratios of precipitating agent NaOH and Na_2CO_3 are between 3.25-5.1 by weight. The calculations of the weights of each chemical substance was based on the chemical reaction reported by Yu et al (1990) and Kuo et al. (1993). The chemical reaction may be described as :

Co-precipitation step :



Calcination step :

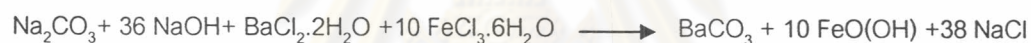


The Dopant levels (x) used in this experiment were: 0.00, 0.25, 0.50, 0.75 and 1.00 and the mole ratio of Fe:Ba is 10

The examples of calculation were as following:

For $x = 0$

Co-precipitation step



The weight of each chemical substance can be calculated as follow,

$$\begin{aligned} \text{Weight of FeCl}_3 \cdot 6\text{H}_2\text{O} &= (\text{amounts of mole of FeCl}_3 \cdot 6\text{H}_2\text{O}) * (1/\% \text{ purity of FeCl}_3 \cdot 6\text{H}_2\text{O}) * \\ &\quad (\text{molecular weight of FeCl}_3 \cdot 6\text{H}_2\text{O}) \\ &= (10) \times (100/99) \times (270.32) = 2730.51 \text{ grams} \end{aligned}$$

We used only one fiftieth for experiment because of the limitation of glassware, so $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ is 54.61 grams. By using the same method, the other chemical substances were calculated.

1. Weight of $\text{BaCO}_3 = ((1) \times (100/99) \times (244.28)) / 50 = 4.935 \text{ grams}$
2. Weight of $\text{NaOH} = ((36) \times (100/98) \times (33.99)) / 50 = 24.97 \text{ grams}$
3. Weight of $\text{Na}_2\text{CO}_3 = (2) \times (100/95) \times (105.99) = 4.463 \text{ grams}$

However, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and NaOH were difficult to weight since they easily hydrate so their actual weights were different from those calculated. As report by Henada et al, the ratio by weigh of NaOH and Na_2CO_3 was 4:1-5:1, so the amount of Na_2CO_3 increased from 2.013 to 4.8934 grams.

For $x=0.25$

Co-precipitation step :



1. $\text{FeCl}_3 \cdot 6\text{H}_2\text{O} = (9.5) \times (0.100/99) \times (270.32) / 50$
 $= 50.8 \text{ (46.416) grams}$
2. $\text{BaCO}_3 = (1) \times (100/99) \times (244.28) / 50$
 $= 4.837 \text{ (4.935) grams}$
3. $\text{CoCl}_2 \cdot 6\text{H}_2\text{O} = 0.25 \times (100/98) \times (237.93) / 50$
 $= 1.213 \text{ (0.836) grams}$
4. $\text{SnCl}_4 \cdot 5\text{H}_2\text{O} = (0.25) \times (100/100) \times (350.58) / 50$
 $= 1.7529 \text{ (1.728) grams}$
5. $\text{NaOH} = (28.5) \times (100/98) \times (33.99) / 50$
 $= 19.770 \text{ (28.12) grams}$
6. $\text{Na}_2\text{CO}_3 = (3.25) \times (0.99) \times (105.99) / 50$
 $= 6.820 \text{ (8.565) grams}$

Remark : () = the actual weight

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Table 3.1 The chemical composition of $\text{BaFe}_{12-2x}\text{Sn}_x\text{Co}_x\text{O}_{12}$ at a variant nominal x

Formula	Chemical	Weight(g)	Absolute mass (mole)
x=0	NaOH	24.485	0.612
	Na_2CO_3	4.834	0.046
	$\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$	4.935	0.020
	$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$	54.608	0.202
X=0.25	NaOH	28.118	0.703
	Na_2CO_3	8.565	0.081
	$\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$	4.935	0.020
	$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$	46.416	0.172
	$\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$	0.836	0.004
	$\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$	1.728	0.005
x=0.50	NaOH	28.117	0.703
	Na_2CO_3	8.565	0.081
	$\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$	4.935	0.020
	$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$	46.416	0.172
	$\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$	1.672	0.007
	$\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$	3.456	0.010
x=0.75	NaOH	28.118	0.703
	Na_2CO_3	7.160	0.067
	$\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$	4.935	0.020
	$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$	46.416	0.172
	$\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$	2.508	0.011
	$\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$	5.187	0.015
x=1.00	NaOH	22.854	0.571
	Na_2CO_3	9.564	0.090
	$\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$	4.933	0.020
	$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$	43.688	0.162
	$\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$	3.344	0.014
	$\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$	6.910	0.020

The solutions of $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ with amounts of mole shown in table 3.1 were first heated and kept at $40 - 50^\circ\text{C}$. Then the mixture solution of $\text{NaOH} / \text{Na}_2\text{CO}_3$ which had been heated to $50 - 55^\circ\text{C}$ was dropped into the former solution. At this stage, when the amount of the former solution increased, brown precipitates formed and the solution became suspended. During the reaction, the temperature was kept at $55 - 60^\circ\text{C}$ in a water bath and the suspension was stirred at 800-1000 rpm by a mechanical stirrer. After the last drop of mixture solution of $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, the suspension was stirred for another 2 hours and the pH was measured. The range of pH was 12-13 as shown in Table 3.2.

Table 3.2 The pH of each nominal x level

Nominal x	pH
0.00	12.57
0.25	12.55
0.50	13.37
0.75	13.71
1.00	13.50

After aging at room temperature for 24 hours, the suspension were filtrated and washed until no chloride was detected by the solution of 10 % by weight of AgNO_3 . The pH then decreased to 9.2-9.4. The precipitate was dried at 60°C in vacuum oven for a few days, grounded in an agate mortar and sieved through 325 mesh. The product of each level of nominal x after firing was 30 - 40 grams.

3.2.2 Firing process

The purpose of firing process is for complete the solid state reaction. However, all dried powder show moisture content $\sim 15 - 20\%$ which we can see from the result of thermal analysis so the first of step of firing was done slowly to achieve the decomposition of the water. For the firing, the dried powders were calcinated in an

electric furnace under an ambient atmosphere at temperature intervals of 50°C , i.e., at $950, 1000, 1050, 1000, 1100, 1150$ and 1200°C with a soaking time of 4 hours each. The profile of the firing at $950 - 1150^{\circ}\text{C}$ is seen in figure 3.1, in which firing time after 750°C increased with increasing time. The firing pattern of the 1200°C specimen is shown in figure. 3.2. The firing time of each sample is about 18 -22 hours which is long enough to complete the reaction without refiring.

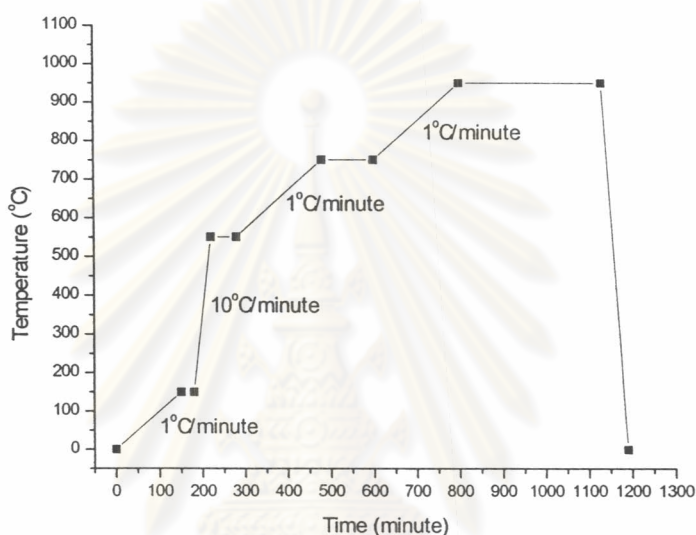


Figure 3.1 The temperature profile of samples calcined at $950-1150^{\circ}\text{C}$

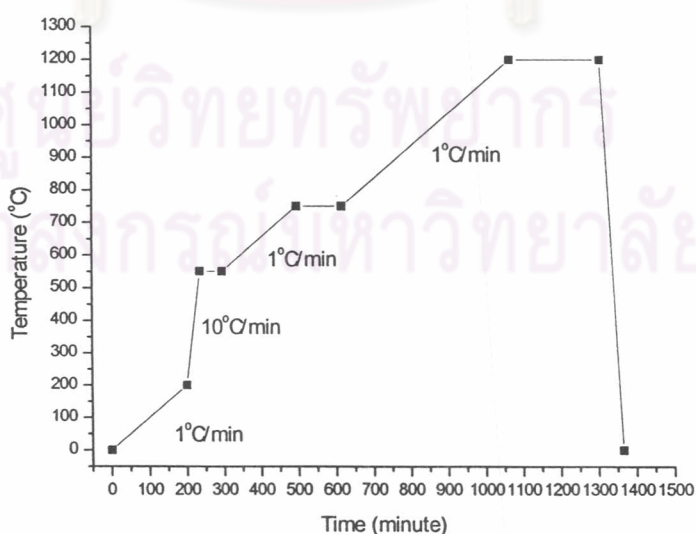


Figure 3.2 The temperature profile of samples calcined at 1200°C

3.3 Characterization

3.3.1 Powder Characterization

3.3.1.1 *Thermal Analysis*

Thermogravimetric and differential thermal analysis (DTA) of the dried powders were carried out on a Netzsch STA 409C in the temperature range 20-1000°C. The heating rate was 10°C/min in Nitrogen(N₂):Oxygen(O₂) = 50:50. Alumina crucible was used as sample holder.

3.3.1.2 *X-ray Diffractometer*

Diffraction patterns of the powders were collected using a Phillip x'pert x-ray diffractometer. The step size was 0.02° (2θ) at a scan time of 1 second per step. The data were analyzed by the PW1876PC-IDENTIFY software. By comparing the pattern with JCPDS standard, the phases were determined. The lattice parameter of the BaFe_{12-2x}Sn_xCo_xO₁₉ were determined by the following relation

Hexagonal,

$$\frac{1}{d^2} = \frac{4}{3} \frac{(h^2 + hk + k^2)}{a^2} + \frac{l^2}{c^2} \longrightarrow 3.1$$

3.3.1.3 *Scanning electron microscope (SEM) and Energy dispersive x-ray(EDX)*

The morphology of calcined powders at 1000-1200°C were examined using Philip XL 30 CP scanning electron microscopy model Phi at 25-30 kV accelerating voltage. Specimens were prepared by dropping and smearing the calcinated powders which were mixed with acetone onto the sample holder to separate the particle. The sample holders were dried at room temperature, and coated with gold-palladium for a few minutes. The resolution of equipment is 3 nm.

The Energy dispersive x-ray (EDX, Linkissis series 300 Oxford instrument) was taken of all samples to determine their chemical composition. The detection limitation of equipment is ~0.2%. The advantage of EDX is that only small amounts of samples are needed.

3.3.1.4 Transmission electron microscope (TEM)

SEM was not capable characterizing the very fine powder fired at 950°C: We, therefore, used that TEM to characterize the powder morphology of these particles. The specimen preparation was as follow:

1. Mix the calcined powders with ethyl alcohol.
2. Shake the mixture until it was well dispersed.
3. Place the mixture on a magnetic stirrer, after a few minutes, the mixture would separate into two layers.
4. Take the suspension of upper layer and then drop it onto 300 mesh copper grid coated with formvar which was placed on a permanent magnet.
5. Dry at room temperature.
6. Characterize these particles by using the JEM-200-CX TEM in bright field mode at magnification typically up to 150,000 using voltage of 100 kV.

Particle size, diameter (d) and thickness (t), were measured from the micrographs of SEM and TEM by using Krumbain diameter (Arai, 1996). The value of surface area (S) and volume (V) were calculated by the following equation (West, 1999).

$$S = 5.196 d^2 + (3 d \times t) \longrightarrow 3.2$$

$$V = 2.598 d^2 \times t \longrightarrow 3.3$$

3.3.2. Magnetic properties.

3.3.2.1 Hysteresisgraph

The vibrating sample magnetometer, VSM (Oxford and Lake Shore 735) of National university of Singapore was used to obtain the hysteresisgraph of calcinated powders. Small quantities of calcinated powder were weighed (about 0.02–0.10 grams)

and packed with aluminum foil. The specimens were then tied to the sample holder of equipment. The magnetic field was then applied in the direction parallel to the samples. The hysteresisgraph of the 1000,1050,1100,1150 and 1200 °C calcinated powder were carried out by using the Oxford machine at maximum field 2 tesla (T), while that of 950°C specimen was carried out by using the Lake Shore VSM at a maximum field 1.50 T. Since the maximum applied field of Lake Shore is 1.50 T, this machine could not be used with sample fired at 1000-1200 °C.

3.3.2.2 Mossbauer measurement

The Mossbauer spectra were obtained using a Mossbauer spectrometer(Canberra model Mr-351). The specimen was prepared by sprinkling the powder between two adhesive tapes. A 50 mC of ^{57}Co in Rh was used as the source of the radiation. The velocity of the machine was calibrated using α -Fe absorber at the room temperature. The spectra were collected in 512 channels, and were resolved by using Pc-Mos II software.

In Figure 3.3 the diagram of preparation, firing and characterization was shown.

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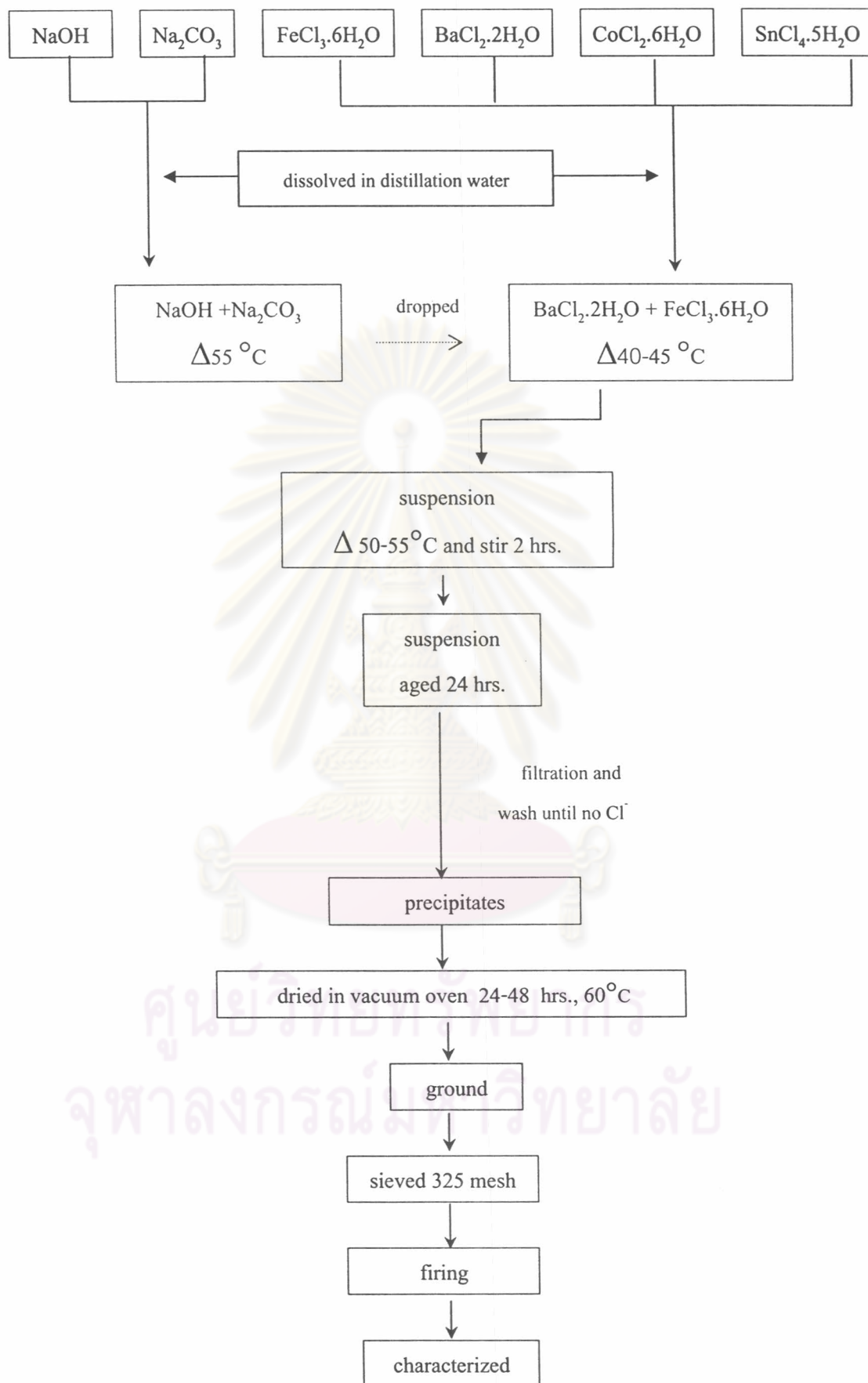


Figure 3.3 The preparation of barium ferrite by co-precipitation technique