CHAPTER 4

RESULTS & DISCUSSION

4.1   Effect of calcination temperatures on the chemical and physical properties.

4.1.1   Undoped specimens.

4.1.1.1 Chemical analysis.

4.1.1.1.1 EDX analysis.

The chemical compositions of the undoped specimens calcined at different temperatures for 4 hours were determined by EDX. The relative amounts of the chemical constituents of each calcined powder are listed in Table 4.1. The amounts of Fe and Ba range from 54.68 to 61.29 and from 4.29 to 4.78 %, respectively. Small amounts of Na (0.67 - 1.08 %) were presented in the powder. These Na ions belong to the residues of the reactions. In addition, Al were also found in the specimen calcined at 1100° C. This could be the result of contamination by the alumna mortar. In the sample fired at 1000 $^{\circ}$C, carbon was detected. The small amount, 0.89 % may be due to the measurement of carbon of sample holder. Other impurities such as Sn, Co and Si were present at levels below 0.1%, which is lower than the detection limits (0.1%) of the EDX. The chemical formulas of the specimens were determined by charge balancing using the valences; Fe (3+), Ba (2+) and O (2-). The chemical formulas of the different specimens are given in Table 4.2. Most of specimens are Fe-rich compared to the stoichiometric composition. The Fe:Ba ratios were between 12.21 and 12.82.   Surig et al. (1996) obtained Fe-rich $BaFe_{13.34}O_{19.17}$ hexaferrites when they used the stoichiometric powder concentration (i.e., Fe_2O_3/BaO ratio = 6.0) and the nearly ideal $BaFe_{11.83}O_{18.89}$ when the ratio was equal to 5.25.

Table 4.1 Relative chemical compositions of undoped specimens soaked for 4 hours at various calcination temperatures

Temperature (°C)	Atomic (%)								
	Fe	Ba	O	Sn	Co	Al	Si	C	Na
950	54.93	4.29	39.69	0.04	-	-	-	-	1.08
1000	54.68	4.46	38.76	0.01	0.06	-	-	0.89	0.93
1100	58.53	4.70	36.50		-	0.18	0.08		-
1500	58.75	4.82	35.83	-	-	-	-	-	0.88
1200	61.29	4.78	33.25	-	-	-	-	-	0.67

Table 4.2 Relative chemical formulas of the undoped specimens soaked for 4 hours at various calcination temperatures

Temperature (°C)	Ratio*			Stoichiometry
	Fe	Ba	O	
950	12.80	1.00	20.21	$BaFe_{12.80}O_{20.21}$
1000	12.26	1.00	19.39	$BaFe_{12.26}O_{19.39}$
1100	12.45	1.00	19.68	$BaFe_{12.45}O_{19.68}$
1150	12.21	1.00	19.32	$BaFe_{12.21}O_{19.32}$
1200	12.82	1.00	20.23	$BaFe_{12.82}O_{20.23}$

* The ratio Fe ,Sn ,Co based on Ba=1 are listed in Table 4.1 .The amounts of O in each sample are determined from the charge balancing.

4.1.1.1.2 TG and DTA.

The curves of TG and DTA are shown in Figure 4.1. During the heating of the precursor mixture, about 17% of the initial mass of the samples were lost at temperatures below 600°C. The weight losses slightly increased (1%) when the temperature was increased to 800°C. This may be due to the decomposition of some

salts such as NaCl. The differential thermal analysis (DTA) showed exothermic peaks at 227.5, 662 and 762.5°C. The first peak was attributed to the transformation of iron hydroxide into oxides. The peaks at 662.2 and 762.5 °C correspond to the formation of BaF. As described by Roose (1980), barium ferrite formation occured at 760°C. Janasi, (2000) report that the barium ferrite peak can be observed at 638 °C in the presence of NaCl.
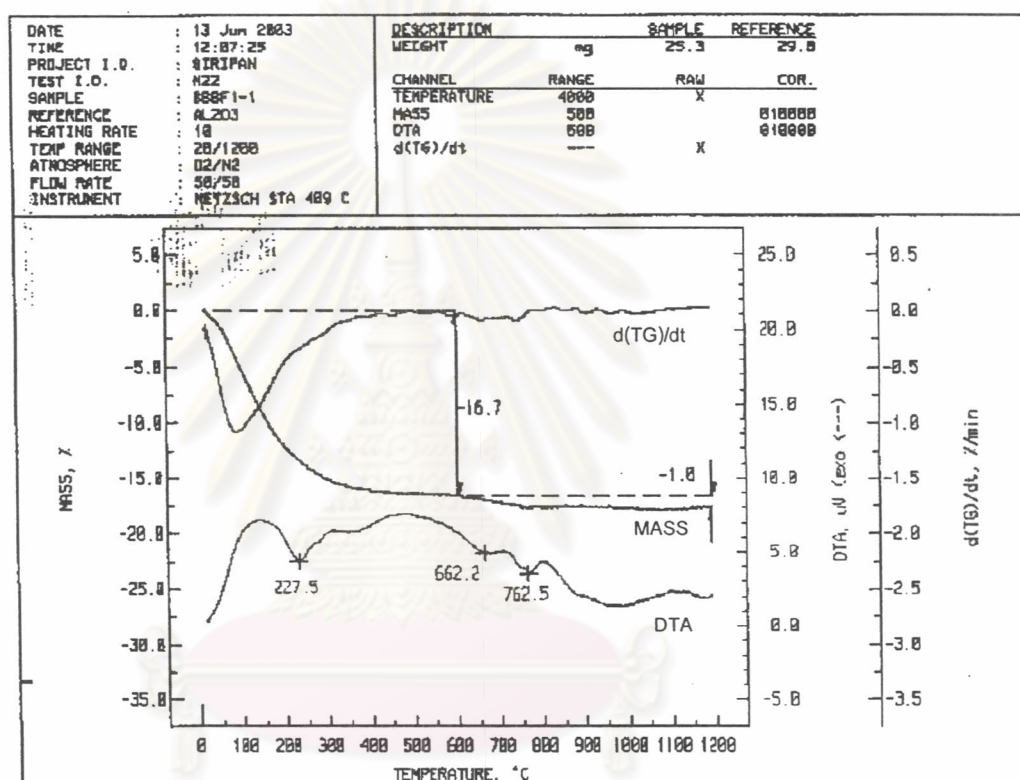

Figure 4.1 The TG and DTA curves for the precursor mixture of undoped samples

4.1.1.1.3 Phase analysis

Figure 4.2 shows the X-ray diffraction (XRD) patterns of the undoped specimens before and after calcination at temperatures between 950 to 1200°C for 4 hours. The specimens before the calcination consist of $BaCO_3$, and a small amount of FeO(OH) (responsible for the peak at $2\theta \approx 28°$ in the XRD pattern). This small peak is caused by very fine particles of this hydroxide. These results corresponded to the chemical reaction which used in calculation done in chapter 3. As the calcination

temperature is raised, α-Fe_2O_3 (an impurity phase) slowly disappears from the BaF, leaving behind more pure BaF. α-Fe_2O_3 often appears as an intermediate phase in the formation of BaF. According to Bahadur et al. (1998), Fe_2O_3 coexists in BaF products even when calcination temperatures of 1100°C is used. This impurity results when some Ba and O are removed by exposure to high temperatures (removal of Ba and O leaves behind $Fe_{12}O_{18}$ (which is 6 moles of Fe_2O_3). Mishra et al. (2004) observed that in Al-doped BaF prepared by the hydothermal-precipitation-calcination method, BaF and α-Fe_2O_3 were presented in their samples heated to 1200°C.

The lattice parameters a and c were obtained by taking the position of the peak (110) and (114) reflection planes, respectively. The values of these lattice parameters for the undoped samples calcined at different temperatures are listed in Table 4.3. The lattice parameter c increased slightly ($\sim$0.5%) as the calcined temperature was raised. However, the lattice parameter a remained the same. The values of a and c were in the ranges of 5.86 to 5.88 angstrom (Å) and 23.14 to 23.21 Å, respectively. The ratios of a : c were between 3.94-3.95 . The increasing of a :c result from the growth of particle in the c axis.
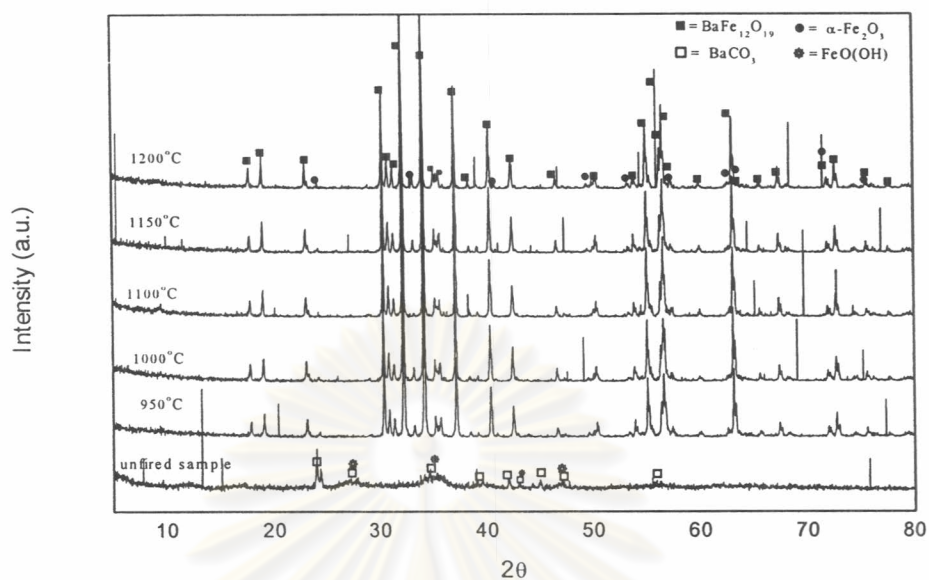
Figure 4.2 The XRD patterns of the undoped BaF soaked for 4 hours at various calcination temperatures

Table 4.3 The lattice parameters a and c of the undoped BaF soaked for 4 hours at various cacination temperatures

Temeperature (°C)	Lattice parameter (Å)		
	a	c	c/a
950	5.86	23.10	3.94
1000	5.87	23.15	3.94
1100	5.87	23.14	3.94
1150	5.87	23.21	3.95
1200	5.88	23.21	3.95

4.1.1.2 Physical properties.

4.1.1.2.1 Particle size, surface area and volume

The diameter (d), thickness (t), surface area, and volume of primary particles of sample were obtained from the micrographs. Their mean values are given in Table 4.4. The average diameters (for each calcination temperature) of the particles

ranged from 83.33 to 881.39 nm. The maximum size particles in each BaF sample increased as calcination temperatures was increased. The largest particle found from samples calcined at temperature 1200° C (diameter = 881.39nm, thickness = 249.69 nm). Janasi et al. reported that the size of BaF prepared by co precipitation was about 0.5 μm when heated between 860 to 1000° C. The surface area and volume were calculate using equation 3.2 and 3.3, respectively. The surface area to volume ratio increased with increase temperature. Their values are in the range of 0.013 - 0.123. As surface area to volume ratio increase, the sizes of the particles also increased.

Table 4.4 Particle size, surface area and volume of undoped specimens soaked for 4 hours at various calcination temperatures

Temperature (°C)	Diameter (nm)	Thickness (nm)	Surface area(nm)^2	Volume (nm)^3	Surface area / Volume
950	83.33	28.20	1.76 x 10^4	14.29 x 10^4	0.123
1000	216.65	91.04	12.01x 10^4	227.55 x 10^4	0.043
1100	312.89	148.64	26.67 x 10^4	945.17x 10^4	0.028
1150	485.55	362.00	77.11 x 10^4	4,943.95 x 10^4	0.016
1200	881.39	249.69	166.94 x 10^4	12,598.80 x 10^4	0.013

4.1.1.2.2 Morphology

Micrographs of the undoped samples soaked at temperatures between 950 and 1200° C are shown in Figure 4.3 (a) to 4.3 (e). As clearly seen, the grains or particles are hexagonal crystals. The sizes are nearly homogeneous. One sees in general that the sizes increase as the calcination temperature is raised.
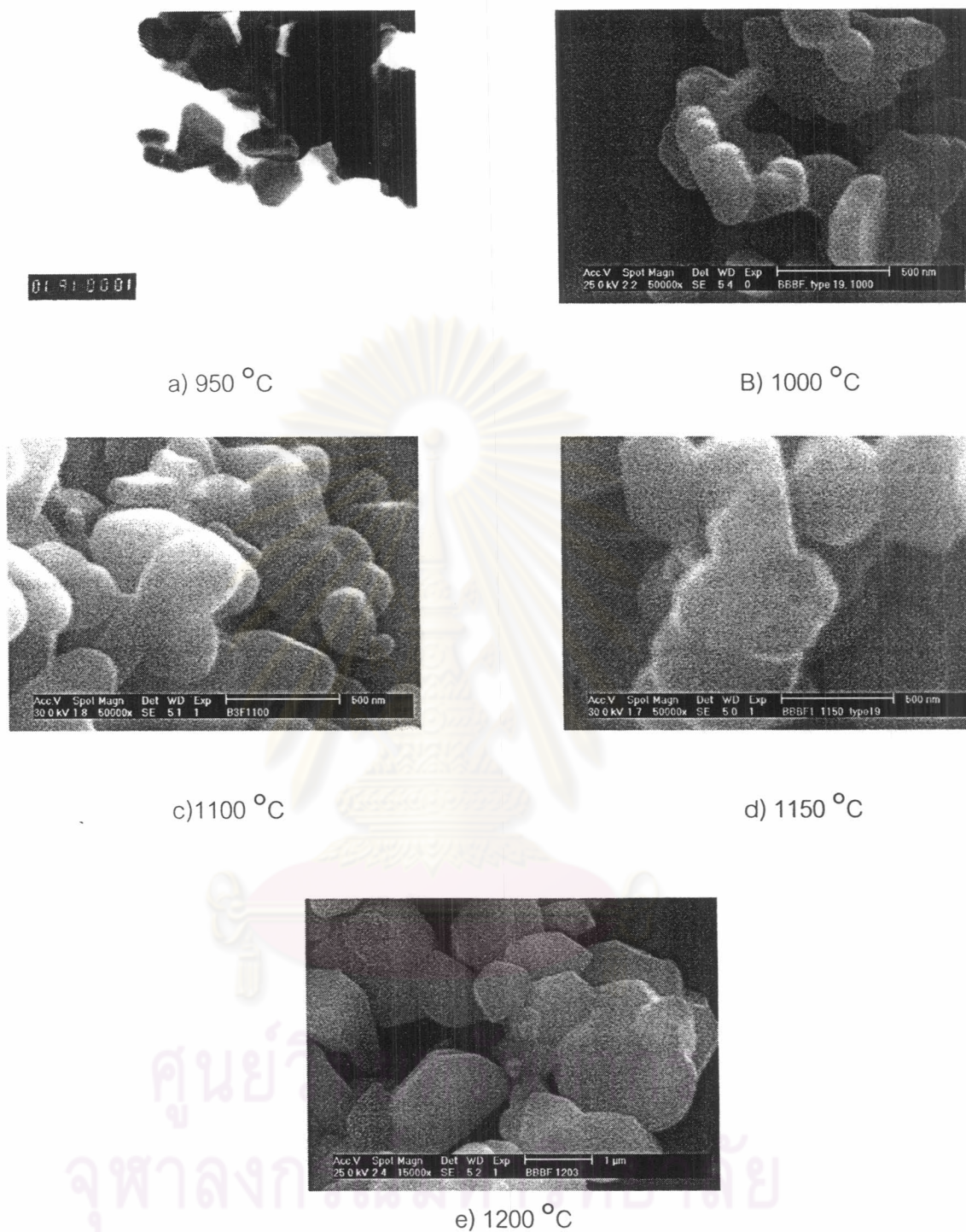
a) 950 °C

B) 1000 °C

c)1100 °C

d) 1150 °C

e) 1200 °C

Figure 4.3 Micrographs of the undoped specimens soaked for 4 hours at various calcinaton temperature (a) 950° C(TEM,150,000X), (b) 1000° C, (c) 1100° C, (d) 1150° C, and (e) 1200° C .(SEM ,b-e,50,000x)

4.1.2 <u>Doped specimens having nominal dopant x = 0.25 level</u>

4.1.2.1 Chemical analysis

4.1.2.1.1 EDX analysis

The atomic percent of doped sample having the nominal x = 0.25 level of dopants calcined at various temperatures are seen in Table 4.5. For calcination temperatures between 950 and 1200 $^{\circ}$C, the amounts of the different elements detected by EDX do not exhibit any systematic variations. However, in the range of 1100 to 1200 $^{\circ}$C, there is a slight increase in the relative amounts of all the chemical constituents. The chemical formulas (based on these relative percentages) are listed in Table 4.6. As we see, the amount of Sn in the calcined samples is less than that of Co. The Ba-rich compositions is found in all specimens. This is needed to obtain better single-phase samples. In stead of a Fe:Ba ratio of 12 to 1, 9-20% more Ba should be added. Surig et al. found that, it is necessary to have a surplus to crystallize the hexaferrite completely at low temperature without intermediate phase.

Table 4.5 Relative chemical compositions for the samples nominal dopant x = 0.25 level soaked for 4 hours at various calcination temperatures

Temperature	Atomic(%)					
($^{\circ}$C)	Fe	Ba	O	Sn	Co	C
950	50.66	4.96	40.23	0.59	2.22	-
1000	50.13	4.88	40.39	0.55	2.17	1.77
1050	52.77	5.08	39.31	0.57	2.24	-
1100	49.69	4.64	39.89	0.56	2.11	3.24
1150	52.34	5.00	39.87	0.57	2.19	-
1200	55.11	5.25	36.82	0.57	2.22	-

Table 4.6 Relative chemical formulas of the samples nominal dopant x = 0.25 level soaked for 4 hours at various calcination temperatures

Temperature (°C)	Ratio*					Formula
	Fe	Ba	Sn	Co	O	
950	10.21	1.00	0.12	0.45	17.01	$BaFe_{10.21}Sn_{0.12}Co_{0.45}O_{17.01}$
1000	10.27	1.00	0.11	0.44	17.08	$BaFe_{10.27}Sn_{0.11}Co_{0.44}O_{17.08}$
1050	10.39	1.00	0.11	0.44	17.25	$BaFe_{10.39}Sn_{0.11}Co_{0.44}O_{17.25}$
1100	10.71	1.00	0.12	0.45	17.76	$BaFe_{10.71}Sn_{0.12}Co_{0.45}O_{17.76}$
1150	10.47	1.00	0.11	0.44	17.37	$BaFe_{10.47}Sn_{0.11}Co_{0.44}O_{17.37}$
1200	10.50	1.00	0.11	0.42	17.39	$BaFe_{10.50}Sn_{0.11}Co_{0.42}O_{17.39}$

* The ratio Fe ,Sn ,Co based on Ba =1 are listed in Table 4.5. The amounts of O in each sample are determined from the charge balancing.

4.1.2.1.2 TG and DTA

The curves are seen in Figure 4.4. The DTA curve shows two distinctive exothermic peaks at 324.4 °C. and 750.9 °C. The major weight losses between room temperature and 200°C are due to the evaporation of water. The transformation of the mixed hydroxides into their oxides is indicated by the exothermic peak at 324.4°C. The BaF formation indicated by the peak at 750.9 °C.
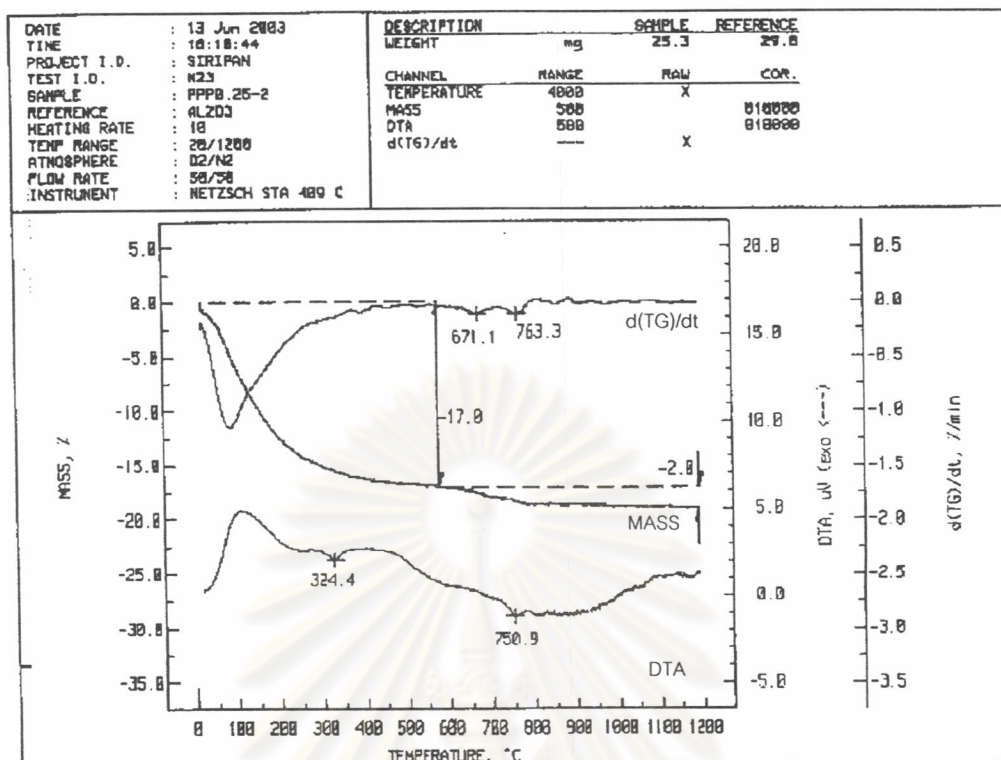
DATE   : 13 Jun 2003
TIME   : 18:18:44
PROJECT I.D. : SIRIPAN
TEST I.O.   : N23
SAMPLE   : PPPB.25-2
REFERENCE   : AL2O3
HEATING RATE : 10
TEMP RANGE : 20/1200
ATMOSPHERE : O2/N2
FLOW RATE   : 50/50
:INSTRUMENT : NETZSCH STA 409 C

DESCRIPTION   SAMPLE REFERENCE
WEIGHT   mg   25.3   29.0

CHANNEL   RANGE   RAW   COR.
TEMPERATURE 4000   X
MASS   500   010000
DTA   500   010000
d(TG)/dt   ----   X

Figure 4.4 TG and DTA curves for the precursor mixture of the sample nominal dopant
x =0.25 level

4.1.2.1.3 Phase analysis

The XRD patterns of doped samples containing the nominal x = 0.25 impurity levels calcined at the different temperatures are shown in Figure 4.5. The samples before calcination consisted of $BaCO_3$ and small amounts of FeO(OH). The FeO(OH) is noticeable in the XRD patterns at $2\theta \approx 28°$. In the samples calcined between 950 and $1200°$ C, both BaF and $Ba_2Fe_{14}O_{22}$ were detected.

The lattice constants **a** and **c** have been determined from the XRD patterns and are listed in Table 4.4. The lattice parameter **a** remains the same (at about 5.87 Å). The value of the lattice parameter **c** increases slightly as the calcination temperature is increased. As the temperature is increased to $1200°$ C, the value of **c** increases from 23.14 to 23.28 Å. The lattice parameters for the sample nominal dopant x = 0.25 level are larger than those of the pure hexagonal ferrites, especially the one calcined at $1150°$ C. The increase is expected since the ionic radii of Co^{2+} (0.82 Å) and

Sn^{4+}(0.71 Å) are larger than that of Fe^{3+} (0.64 Å). The oxides of Co and Sn are not seen in any the XRD patterns.

Table 4.7 The lattice parameters **a** and **c** in the samples nominal dopant x = 0.25 level soaked for 4 hours at various calcination temperatures

Temperature (°C)	Lattice parameters(Å)		
	a	c	c/a
950	5.87	23.20	3.95
1000	5.87	23.14	3.94
1050	5.87	23.18	3.95
1100	5.87	23.21	3.95
1150	5.87	23.17	3.95
1200	5.87	23.28	3.97
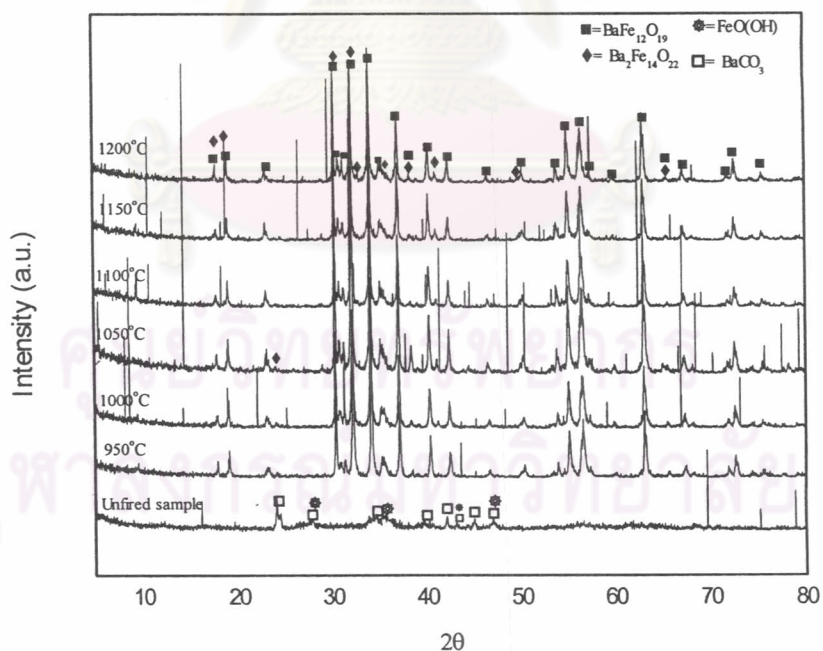
Figure 4.5 The XRD patterns in the samples nominal dopant x = 0.25 level soaked for 4 hours at various calcination temperatures

4.1.2.2   Physical properties

4.1.2.2.1 Particle size, surface area and volume

The values of the diameter and the thickness for the samples nominal dopant x = 0.25 doped level are listed in Table 4.8. As the calcination temperature is increased, one sees that diameter increases from 99.50 to 956.nm and that thickness increases from 33.40 to 279.92 nm. From the analysis of the micrographs, the surface areas were seen to range from 2.28×10^{-4} to 199.09×10^{-4} nm^2. The ratio of surface area to volume decrease with increasing temperature.

Table 4.8 Particle size ,surface area , and volume for the samples nominal dopant x = 0.25 level soaked for 4 hours at various calcination temperatures

Temperature (°C)	Diameter (nm)	Thickness (nm)	Surface area $(nm)^2$	Volume $(nm)^3$	Surface area/ Volume
950	99.50	33.40	2.28×10^4	21.48×10^4	0.106
1000	163.41	70.87	6.94×10^4	122.92×10^4	0.056
1050	237.41	86.18	13.46×10^4	315.48×10^4	0.043
1100	334.85	146.44	29.28×10^4	$1,066.48 \times 10^4$	0.027
1150	682.47	274.09	$116.62.1 \times 10^4$	$8,291.86 \times 10^4$	0.014
1200	956.27	279.92	199.09×10^4	$16.625.97 \times 10^4$	0.012

4.1.2.2.2 Morphology

The TEM and SEM images of the sampes nominal dopant x = 0.25 level are seen in Figures 4.6(a) to 4.6(f). As seen, the sizes of the particles increased as higher calcination temperatures were used. The average dimensions of the particles are listed in Table 4.8. The observed shapes are those of the hexagonal crystals. The sizes are rather homogeneous and appear to increase in size as the calcination temperature is increased.
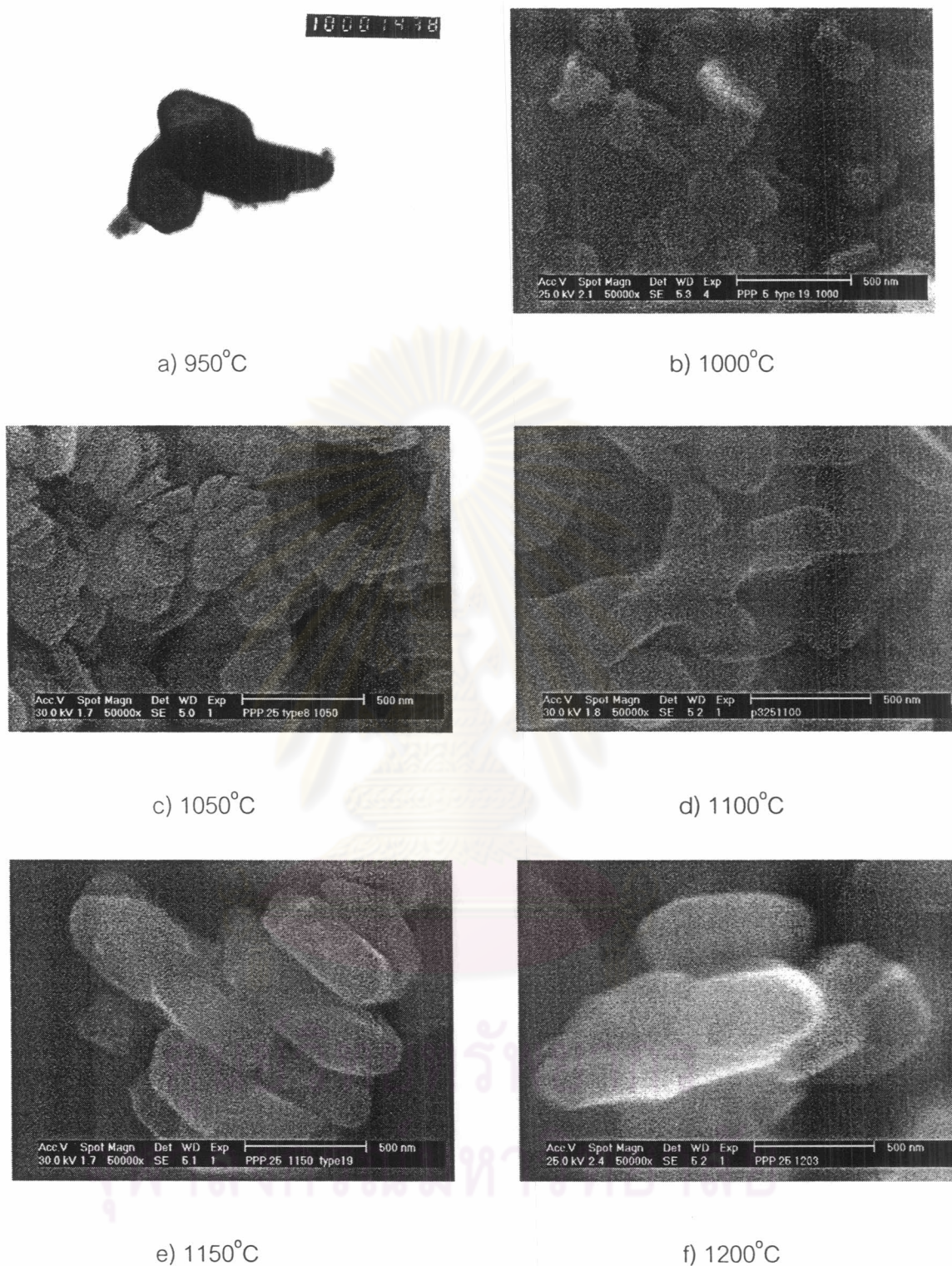
a) 950°C

b) 1000°C

c) 1050°C

d) 1100°C

e) 1150°C

f) 1200°C

Figure 4.6 Micrographs of the samples nominal dopant x = 0.25 level soaked for 4 hours

at various calcination temperatures (a) 950°C (TEM, 150,000X) (b) 1000°C

(c) 1050°C, (d) 1100°C, (e) 1150°C and (f) 1200°C (b-e,SEM,50,000X)

4.1.3 Doped specimens having nominal dopant x = 0.5 level

4.1.3.1 Chemical analysis

4.1.3.1.1 EDX analysis

The atomic percentage of doped sample having the nominal x = 0.5 levels of dopants calcination at various calcination temperatures were determine by EDX. The relative amounts of the chemicals in the calcined samples are listed in Table 4.9. The compositions of the samples ranged as follows: Fe, from 47.85 to 52.40; Ba, from 4.18 to 4.73; Sn, from 1.91 to 2.36 and Co from 1.91 to 2.13 %. The Fe to Ba ratio ranged from 10.86 to 11.63. The starting Fe:Ba ratio was 8.6. The loss of Ba, causing the increasing of Fe: Ba ratio of all samples can be accounted for the differences in the stability of the precipitates ($BaCO_3$, $FeO(OH)$ and $\gamma\text{-}Fe_2O_3$ as determine by the XRD patterns). The stability constants (K_{SP}) of $BaCO_3$ is 2.58×10^{-9} (West, 1987), $FeO(OH)$ and $\gamma\text{-}Fe_2O_3$ are a rather stable colloid. The ratio of Fe:Ba for preparing $BaFe_{12}O_{19}$ by the co-precipitation method is not well established. There is some uncertainty of what the ratio should be for preparing the doped BaF by this method. The ratio should be somewhere in the range between 10 and 11.5 (Haneda, Roose, Surig et al.and Chen et al.1998).

Table 4.9 Relative chemical compositions for the samples nominal dopant x = 0.50 level soaked for 4 hours at various calcination temperatures

Temperature	Atomic(%)						
(°C)	Fe	Ba	O	Sn	Co	Al	Si
950	51.38	4.73	39.10	2.36	2.14	0.18	0.12
1000	47.85	4.18	43.86	1.91	1.91	0.18	0.11
1050	48.02	4.30	43.40	2.01	1.96	0.18	0.13
1100	49.83	4.38	42.11	1.97	2.03	0.19	0.08
1150	52.40	4.70	38.38	2.10	2.13	0.17	0.12
1200	51.33	4.41	39.96	1.94	2.02	0.24	0.10

Table 4.10 Relative chemical formulas of the samples nominal dopant x = 0.50 level
soaked for 4 hours at various calcination temperatures

Temperature ($^{\circ}$C)	Ratio*					Formula
	Fe	Ba	O	Sn	Co	
950	10.86	1.00	18.90	0.49	0.46	$BaFe_{10.86}Sn_{0.49}Co_{0.46}O_{18.90}$
1000	11.45	1.00	19.54	0.46	0.46	$BaFe_{11.45}Sn_{0.54}Co_{0.45}O_{19.54}$
1050	11.17	1.00	19.14	0.47	0.46	$BaFe_{11.17}Sn_{0.47}Co_{0.46}O_{19.14}$
1100	11.39	1.00	19.45	0.45	0.46	$BaFe_{11.39}Sn_{0.45}Co_{0.46}O_{19.45}$
1150	11.14	1.00	19.06	0.45	0.45	$BaFe_{11.14}Sn_{0.45}Co_{0.45}O_{19.06}$
1200	11.63	1.00	19.79	0.44	0.46	$BaFe_{11.63}Sn_{0.44}Co_{0.46}O_{19.79}$

* The ratio of Fe,Sn, Co based on Ba=1 are listed in Table 4.9. The amounts of O in each sample are determined from charge balancing.

4.1.3.1.2   TG and DTA

The curves of TG and DTA are seen in Figure 4.7. The TG curve shows a total weight loss of 18.3% when the samples are heated up to 750° C. The major losses occur as the specimens are heated up to 300°C. This corresponds to the evaporation of water and decompositions of some iron hydroxides such as FeO(OH). The DTA curves exhibit exothermic reaction peak when the $BaFe_{12}O_{19}$ begins to form (Roose).
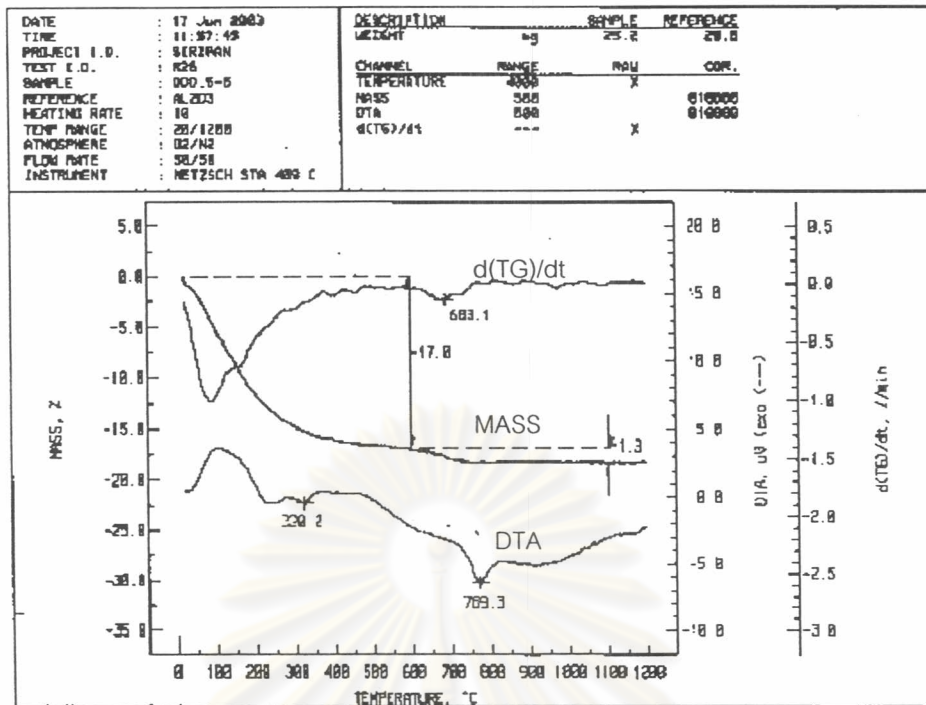
Figure 4.7   TG and DTA curves for the precursor mixture of the sample nominal

dopant x = 0.50 level

4.1.3.1.3 Phase analysis

The XRD patterns of doped samples containing the nominal x = 0.5 dopant levels calcination at the different temperatures are seen in Figure 4.8.   The samples before calcination consisted of $BaCO_3$ γ-Fe_2O_3 and FeO(OH). At cacination temperatures up to 1000° C, most samples consist of BaF with a small amount of γ-Fe_2O_3 . As the temperature is increased up to 1200° C, some γ-Fe_2O_3 remains in these doped BaF. The oxide of Co ad Sn can not be detected in any of the XRD patterns of these BaF.

The lattice constant **a** and **b** have been determined from the XRD patterns. The lattice parameter **a** range between 5.87 to 5.90 Å as the calcination temperature is increased from 1000 to 1200°C. Cacination in the same temperature range ,the lattice parameter c increases from 23.21 to 23.28 Å. The lattice parameters for the nominal x = 0.5 doped BaF are larger than those of the pure and lightly doped (nominal x = 0.25 levels) hexagonal ferrites.

Table 4.11 The lattice parameters **a** and **c** in the samples nominal dopant x = 0.5 level

soaked for 4 hours at various cacination temperatures

Temperature($^{\circ}$c)	Lattice parameters (Å)		
	a	c	c/a
950	5.88	22.73	3.87
1000	5.89	23.21	3.94
1050	5.89	23.27	3.95
1100	5.88	23.25	3.95
1150	5.90	23.28	3.95
1200	5.89	23.28	3.95
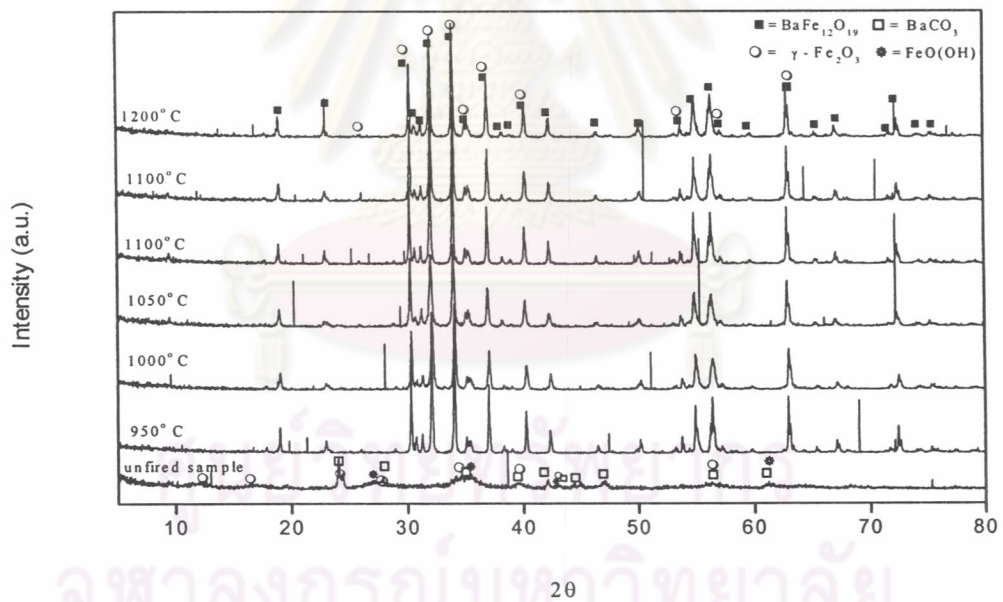
Figure 4.8 XRD patterns of the samples nominal dopant x = 0.5 level soaked for 4 hours

at various calcination temperatures

4.1.3.2 Physical properties

4.1.3.2.1 Particle size , surface area and volume

The diameter (d) and the thickness (t) were measured from the TEM and SEM micrograhs of the powder in the ways described in Chapter 3. The values of the diameter and the thickness for the samples nominal dopant x = 0.5 level are listed in Table 4.12. As the calcination temperatures increased, one sees that d is in the range 117.50 to 481.06 nm and that t is in the range 25.00 to 169.83 nm. Calculating the ratio S/V (also listed in Table 4.12), we see that S/V decreases as the calcination temperature increases. The S/V decrease with the grain size increase.

Table 4.12 Particle size, surface area and volume for the samples nominal dopant x = 0.5 level soaked for 4 hours at various calcination temperatures

| Temperature (^{o}C)	Diameter (nm)	Thickness (nm)	Surface (nm)^2	Volume (nm)^3	Surface / Volume
950	117.50	25.00	2.67×10^4	22.42×10^4	0.119
1000	191.70	82.00	9.49×10^4	195.73×10^4	0.048
1050	279.64	75.15	16.46×10^4	381.70×10^4	0.043
1100	237.29	79.00	12.94×10^4	288.92×10^4	0.045
1150	337.46	83.26	23.22×10^4	615.85×10^4	0.038
1200	481.06	169.83	54.57×10^4	$2,552.73 \times 10^4$	0.021

4.1.3.2.2 Morphology

Figure 4.9 a) – f) show the TEM and SEM images.The structures of the particles show typical hexagonal crystal of BaF. Theirs size are homogeneous. With increasing the temperature, the particle size increase. The particles show the direction of c parallel to the page.
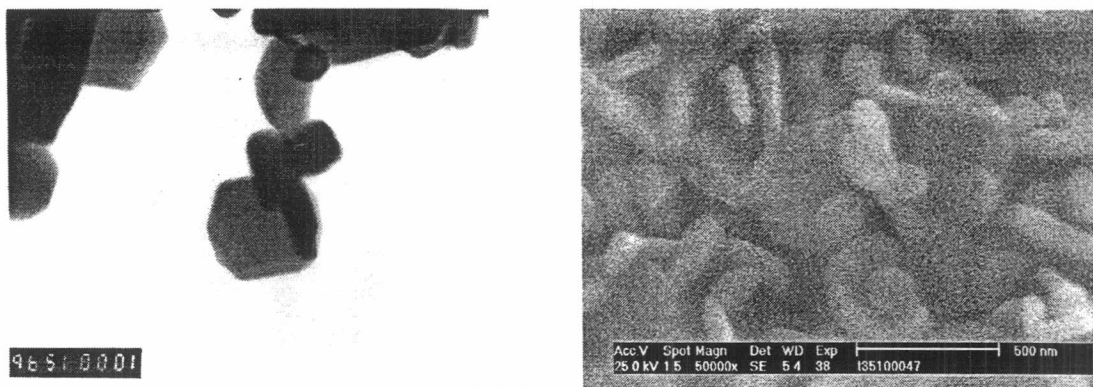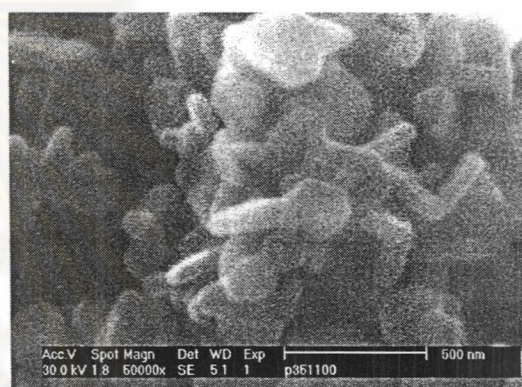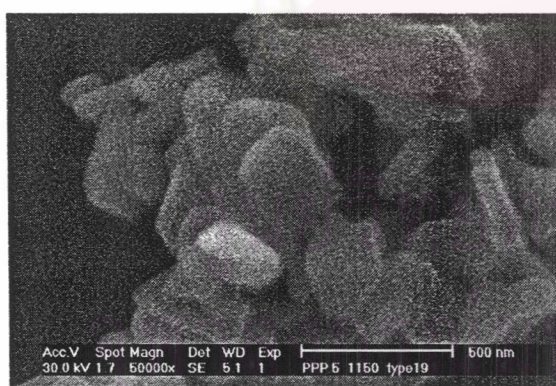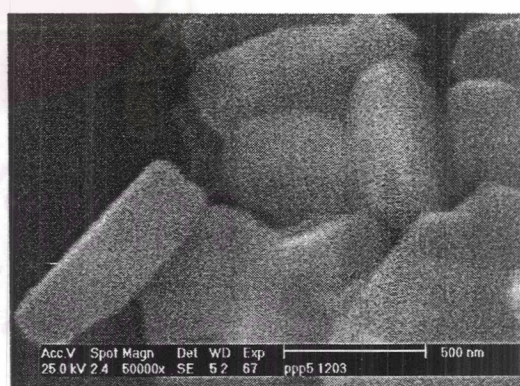
a) 950°C

b) 1000°C
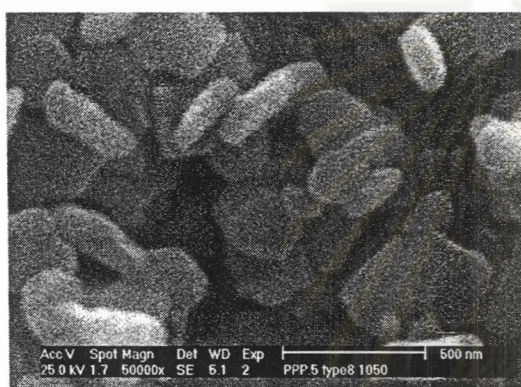
c) 1050°C

d) 1100°C

e) 1150°C

f) 1200°C

Figure 4.9 Micrographs of the samples nominal dopant x = 0.5 level soaked for 4 hours at various calcination temperatures (a) 950°C (TEM, 150,000X). (b) 1000°C, (c) 1050°C, (d) 1100°C, 1150°C, and 1200°C.(SEM,b-e,50,000X)

4.1.4 Doped specimens with nominal x value = 0.75

4.1.4.1 Chemical analysis

4.1.4.1.1 EDX analysis

The chemical compositions of samples calciantion at 950-1200°C when the nominal x value is 0.75 are shown in Table 4.13. The atomic percentages of the samples were measured by EDX. Their chemical formulas are shown in Table 4.14. The total content of Fe, Ba, Sn and Co range from in 41.84 – 46.86%, 4.41 – 4.57%, 2.74 – 2.94% and 2.93 – 3.07% respectively. All samples contain Na residues except for the one fired at 1000°C.This may be due the measurement error. As shown in Table 4.14, the ranges of the amount of constituents in specimens were Fe 10.25 to 10.47, Sn 0.62-0.64 Co, 0.64-0.67 and O: 18.24-18.60. Every sample showed Ba-rich compared to the stoichiometry. This result corresponded to the nominally doped x = 0.25 and x = 0.50 samples. This result has been described in the section 4.1.1.1.1.

Table 4.13 Relative chemical compositions of the samples nominal x value = 0.75
soaked for 4 hours at the various calcination temperatures

Temperature (^{o}C)	Atomic(%)						
	Fe	Ba	O	Sn	Co	C	Na
950	46.86	4.53	42.36	2.88	3.07	-	0.65
1000	46.15	4.41	40.11	2.74	2.94	3.63	-
1050	46.03	4.49	42.90	2.89	2.93	-	0.67
1100	46.82	4.55	42.04	2.89	2.97	-	0.67
1150	45.98	4.51	42.93	2.94	2.90	0.10	0.61
1200	41.84	4.57	41.30	2.82	3.02	-	0.51

Table 4.14 Relative chemical formulas of the samples nominal x value = 0.75 soaked for

4 hours at the various calcination temperatures

Temperature (°C)	Ratio*					Formula
	Fe	Ba	O	Sn	Co	
950	10.34	1.00	18.47	0.64	0.68	$BaFe_{10.34}Sn_{0.64}Co_{0.68}O_{18.47}$
1000	10.46	1.00	18.61	0.62	0.67	$BaFe_{10.46}Sn_{0.62}Co_{0.67}O_{18.61}$
1050	10.25	1.00	18.32	0.64	0.65	$BaFe_{10.25}Sn_{0.64}Co_{0.65}O_{18.32}$
1100	10.29	1.00	18.36	0.64	0.65	$BaFe_{10.29}Sn_{0.64}Co_{0.65}O_{18.36}$
1150	10.20	1.00	18.24	0.65	0.64	$BaFe_{10.25}Sn_{0.65}Co_{0.64}O_{18.24}$
1200	10.47	1.00	18.60	0.62	0.66	$BaFe_{10.47}Sn_{0.62}Co_{0.66}O_{18.60}$

* The ratios Fe, Sn, Co based on Ba=1 are listed in Table 4.13. The amounts of O in each sample are determined from the charge balancing.

4.1.4.1.2 TG and DTA

The curve of TG and DTA are seen in Figure 4.10. The total weight losses of these doped-specimens are about 16.2%. Endothermic reaction occurred at 100°C due to the evaporation of physical absorption water. At temperature 750 °C, there is exothermic reaction due to the formation of precursor salt of BaF as explained in the previous section.

DATE : 24 Nov 2003
TIME : 13:15:43
PROJECT I.D. : SIRIPAN
TEST I.D. : M4B
SAMPLE : DOD.75
REFERENCE : AL2O3
HEATING RATE : 10
TEMP RANGE : 20/1200
ATMOSPHERE : O2/N2
FLOW RATE : 50/50
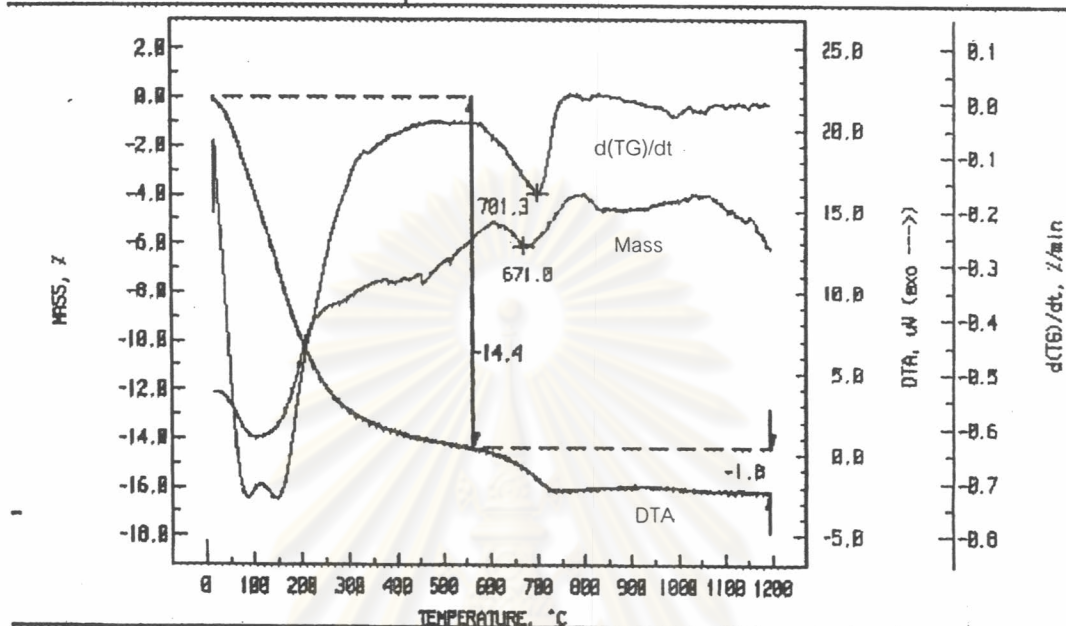INSTRUMENT : NETZSCH STA 409 C

Figure 4.10 The TG and DTA curves for precursor mixture of the sample nominal x value = 0.75

4.1.4.1.3 Phase analysis

The XRD patterns of samples having the nominal doping level of x = 0.75 calcined at different temperatures are similar to those in the patterns of in the previous section. The unfired sample consists of $BaCO_3$, γ-Fe_2O_3 and $FeO(OH)$. The pattern are shown in Figure 4.11 .As the calcination temperature was increased, the XRD pattern began to show the lines belonging to $BaFe_{12}O_{19}$ with weak line belonging to γ-Fe_2O_3. The lattice parameters of these samples are given in Table 4.15. The values of a and c range between 5.88 and 5.89Å and between 23.24 and 23.34 Å, respectively. Comparatively, the lattice parameters of samples having a nominal doping of 0.75 are larger than those of the undoped sample and of the doped samples having the nominal compositions 0.25 and 0.50.
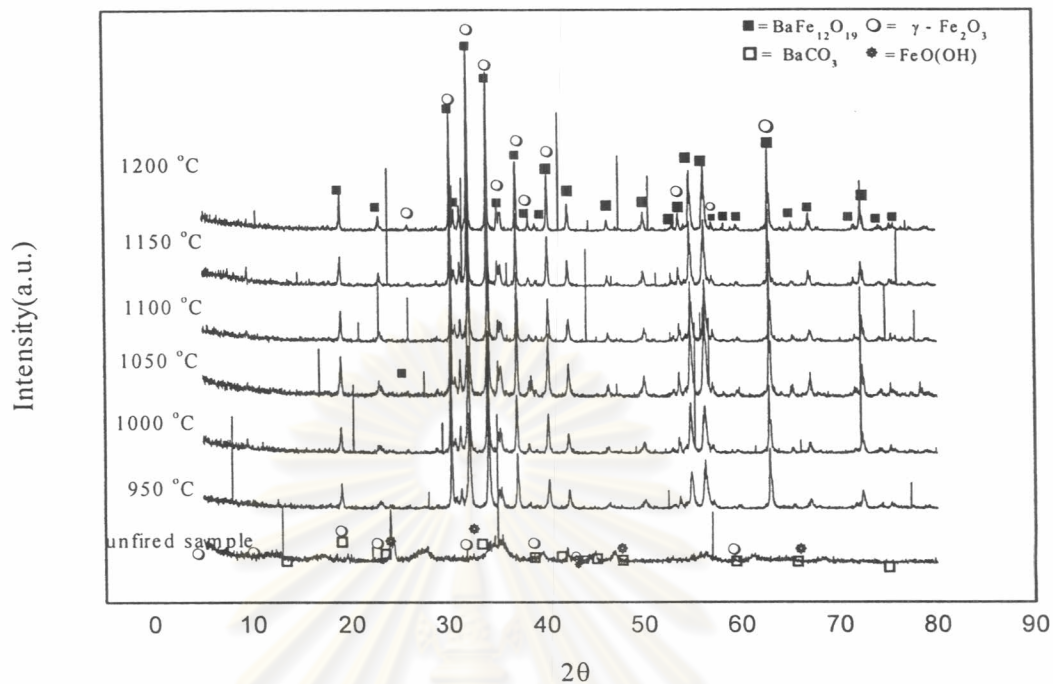
Figure 4.11 The XRD pattern of the samples nominal x value =0.75 soaked for 4 hours
at various calcination temperatures

Table 4.15 The lattice parameters a and c of the samples nominal x value =0.75
soaked for 4 hours at various calcination temperatures

Temperatures(°C)	Lattice parameters(Å)		
	a	c	c/a
950	5.88	23.24	3.95
1000	5.89	23.20	3.94
1050	5.89	23.28	3.95
1100	5.89	23.26	3.95
1150	5.89	23.34	3.96
1200	5.89	23.31	3.96

4.1.4.2 Physical properties

4.1.4.2.1 Particle size, surface area and volume

The measurement of the particle size was done on the TEM and SEM micrographs taken from each specimen. The surface area and volume of particles and ratios of surface area to volume (S/V) are given in Table 4.16. The diameters and thickness are between 122.50 and 924.29 nm and between 28.50and 313.36 nm, respectively. The values of the surfaces area, the volumes and S/V ratios are between 3.00×10^4 and 204.94×10^4 nm^2, between 27.78×10^4 and $18,187.19 \times 10^4$ nm^{3}and between 0.011-0.108 and 0.053, respectively.

Table 4.16 Particle size, surface area and volume of the samples nominal x value =0.75 soaked for 4 hours at various calcination temperatures

| Temperature ($^\circ$C)	Diameter (nm)	Thickness (nm)	Surface area (nm)^2	Volume (nm)^3	Surface area /Volume
950	122.50	28.50	3.00×10^4	27.78×10^4	0.108
1000	215.77	69.88	10.57×10^4	211.31×10^4	0.050
1050	217.91	62.93	10.94×10^4	224.93×10^4	0.049
1100	268.46	79.69	11.78×10^4	256.96×10^4	0.046
1150	268.46	82.93	16.04×10^4	388.21×10^4	0.041
1200	945.29	313.36	204.94×10^4	$18,187.19 \times 10^4$	0.011

4.1.4.2.2 Morphology

The images from TEM and SEM for samples calcined at various temperatures are shown in Figure. 4.12 a) – 4.12 f). All samples have the hexagonal crystals and similar particle sizes. As the temperature increases, the particle size also increases. This is corresponding to the decreasing of S/V ratios.
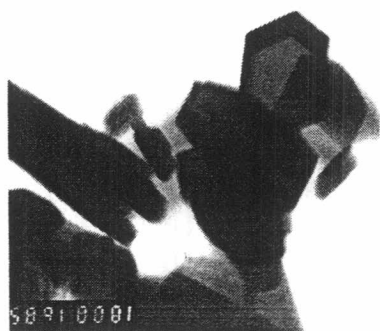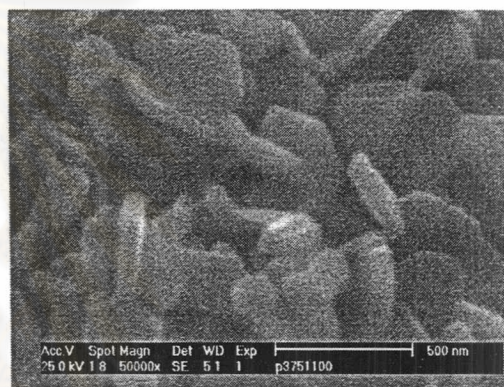
a) 950 °C
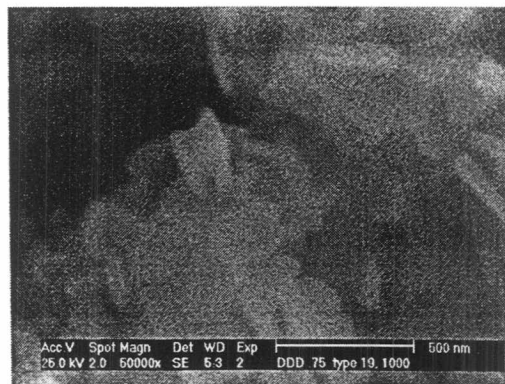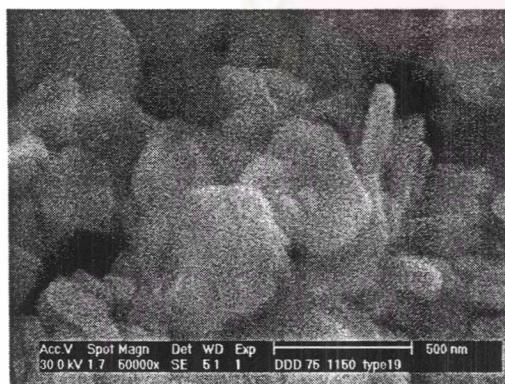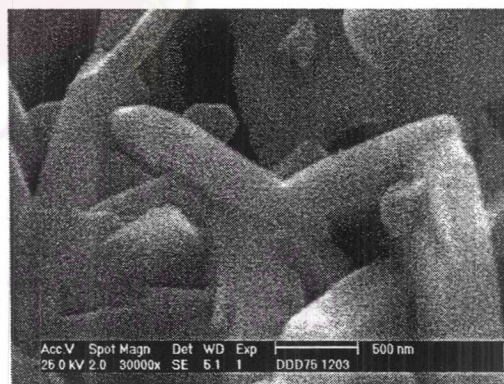
b)1000 °C
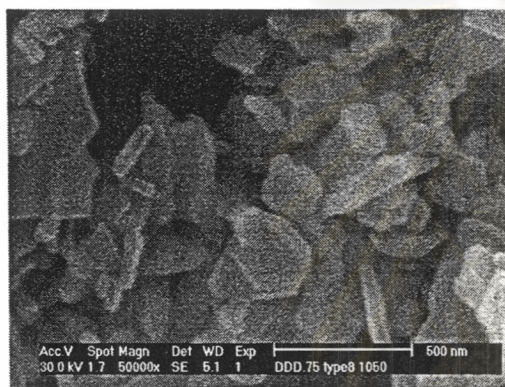
c) 1000 °C

d) 1100 °C

e) 1150 °C

f) 1200 °C

Figure 4.12 Micrographs of the samples nominal x value =0.75 soaked for 4 hour at
various cacination temperatures a) 950 °C, (TEM,150,000X) b) 1000 °C,
c) 1050 °C, d) 1100 °C, e) 1150 °C and f) 1200 °C,(SEM,b-e, 50,000X)

4.1.5 Doped specimens with nominal dopant level of x value = 1.00

4.1.5.1 Chemical analysis

4.1.5.1.1 EDX analysis

The chemical compositions of samples calcineded at 950-1200°C when the nominal x value is 1.00 are shown in Table 4.17. The atomic percentage of the samples was measured by EDX. Their chemical formulas are shown in Table 4.18. All samples contained Na (0.38-0.58%) residues. Every sample was Ba-rich comparing to Ba in the stoichiometry. The Fe:Ba ratios ranged from 9.52 to 10.16.

Table 4.17 Relative chemical compositions of the samples nominal dopant level of x =1.00 soaked for 4 hours at the various cacination temperatures

Temperature	Atomic(%)						
(°C)	Fe	Ba	O	Sn	Co	C	Na
950	42.84	4.47	43.38	4.16	3.85	0.77	0.52
1000	39.54	4.11	44.28	3.81	3.50	4.76	-
1050	46.95	4.80	39.35	4.23	4.12	0.23	0.49
1100	45.03	4.43	41.03	3.92	4.05	1.15	0.38
1150	46.72	4.74	39.77	4.30	4.15	-	0.54
1200	39.61	4.16	44.79	3.94	3.51	3.42	0.58

Table 4.18 Relative chemical formulas of the samples nominal dopant level of x = 1.00

soaked for 4 hours at various calcination temperatures

Temperature	Ratio*					Formula
(°C)	Fe	Ba	O	Sn	Co	
950	9.58	1.00	18.10	0.93	0.86	$BaFe_{9.58}Sn_{0.93}Co_{0.86}O_{18.10}$
1000	9.62	1.00	18.14	0.93	0.85	$BaFe_{9.62}Sn_{0.93}Co_{0.85}O_{18..14}$
1050	9.78	1.00	18.29	0.88	0.86	$BaFe_{9.78}Sn_{0.88}Co_{0.86}O_{18.29}$
1100	10.16	1.00	18.93	0.88	0.91	$BaFe_{10.16}Sn_{0.88}Co_{0.91}O_{18.93}$
1150	9.86	1.00	18.47	0.91	0.88	$BaFe_{9.86}Sn_{0.91}Co_{0.88}O_{18.47}$
1200	9.52	1.00	18.02	0.95	0.84	$BaFe_{9.52}Sn_{0.95}Co_{0.84}O_{18.02}$

* The ratios of Fe, Sn, Co based on Ba=1 are listed in Table 4.17. The amounts of O in each sample are determined from the charge balancing.

4.1.5.1.2 TG and DTA

The TG and TGA curves are seen on Figure 4.13. During the heating of the precursor, about 13 % of the initial mass was lost. This was due to the evaporation of water. An exothermic peak occurred at 778 °C due to the formation of BaF. The temperature of BaF formation was slightly higher than previous sample. Panov et al. (1993) found that the crystallization temperature of barium ferrite increased when the concentration of Co and Ti increased.
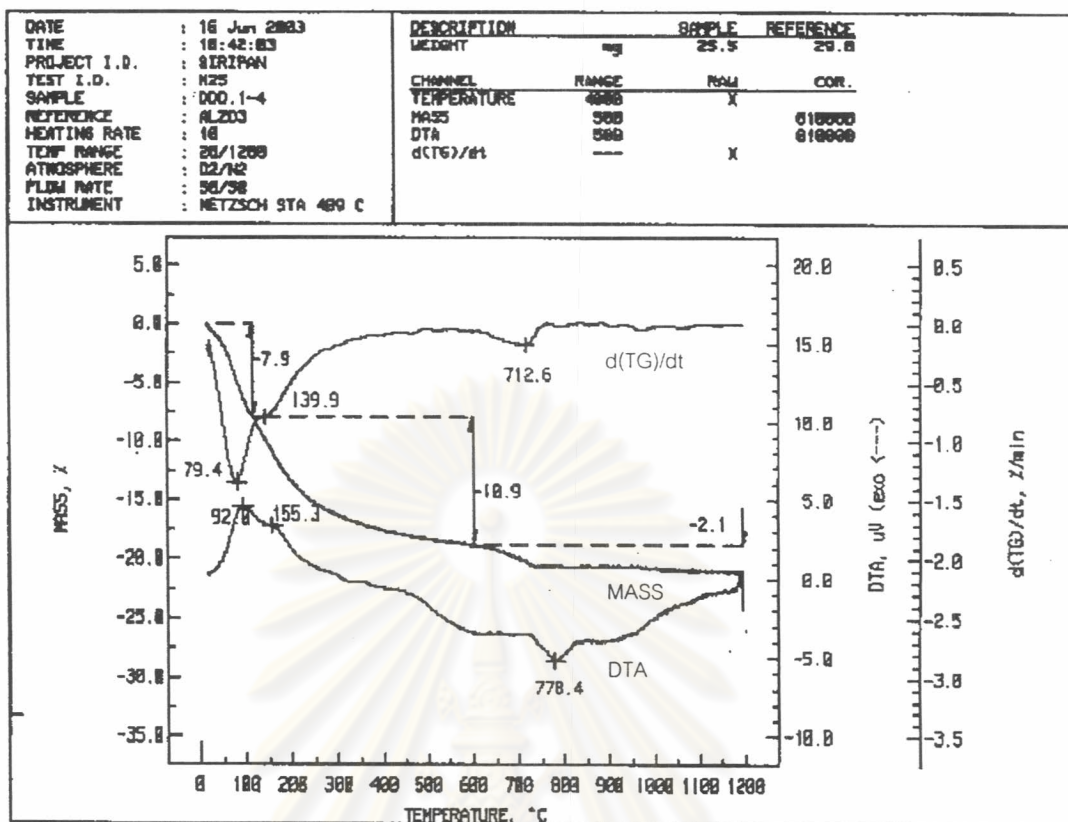
Figure 4.13 The TG and DTA for precursor mixture of the samples nominal dopant level
of x = 1.00

4.1.5.1.3. Phase analysis

The XRD patterns of samples having the nominal doping level of
x = 1.00 calcined at different temperatures are shown in Figure 4.14 . The unfired
sample consists of $BaCO_3$, γ-Fe_2O_3 and FeO(OH). The patterns are seen in Figure 4.14.
At 950-1200 $^\circ$C, the XRD pattern show $BaFe_{12}O_{19}$ and γ-Fe_2O_3 in all the samples expept
the 1000°C sample. In this,α-Fe phase appeared. The lattice parameters of these
samples are given in Table 4.19. The values of a and c range between 5.88 and 5.91 Å
and between 23.30 and 23.44 Å, respectively. There were no systematic changes in
either a or c with the increase in the calcination temperature. Comparatively, the lattice
parameters having a nominal doping of 1.00 are larger than those of all the lower doped
samples.
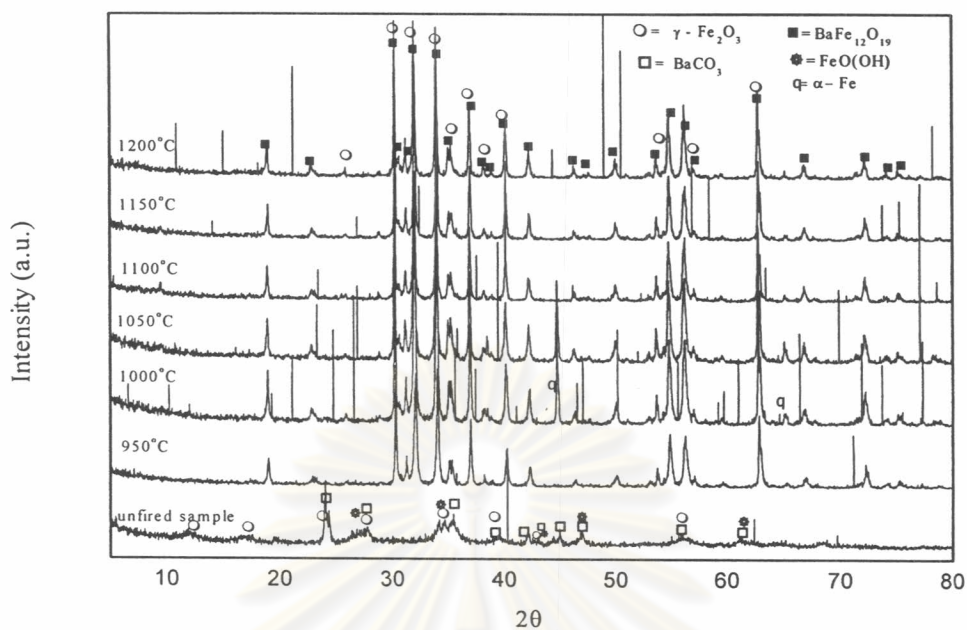
Figure 4.14 The XRD pattern of the samples nominal dopant level of x = 1.00 soaked for 4 hours at various calcination temperatures

Table 4.19 The values of the lattice parameters a and c of the samples nominal dopant level of x = 1.00 soaked for 4 hours at various calcination temperatures

Temperature($^\circ$c)	Lattice parameters (Å)		
	a	c	c/a
950	5.88	23.44	3.99
1100	5.89	23.33	3.96
1050	5.91	23.38	3.96
1100	5.90	23.38	3.96
1150	5.89	23.30	3.96
1200	5.90	23.34	3.96

4.1.5.2   Physical properties

4.1.5.2.1. Particle size , surface area and volume

The measurements of the particle size were done on theTEM and SEM micrographs taken of each specimen. The surface area and volume of particles and ratios of surface area to volume (S/V) are given on Table 4.20. The diameters and thickness are between 90 and 224.46 nm and between 27.50 and 78.18 nm, respectively. The values of the surfaces, the volumes and S/V ratios are between 1.79 and 11.81×10^4 nm^2, between 14.47×10^4 and 255.84×10^4 nm^3 and between 0.046 and 0.124, respectively.

Table 4.20 Particle size, surface area, and volume for the samples nominal dopant level of x = 1.00 soaked for 4 hours at various calcination temperatures

Temperature (^{o}C)	Diameter (nm)	Thickness (nm)	Surface $(nm)^2$	Volume $(nm)^3$	Surface / Volume
950	90	27.50	1.79×10^4	14.47×10^4	0.124
1000	166.73	71.17	7.17×10^4	128.50×10^4	0.056
1050	206.79	71.20	9.97×10^4	197.76×10^4	0.050
1100	211.17	72.19	10.37×10^4	209.09×10^4	0.050
1150	213.18	77.47	10.86×10^4	228.67×10^4	0.047
1200	224.46	78.18	11.81×10^4	255.84×10^4	0.046

4.1.5.2.2 Morphology

The images from TEM and SEM for samples calcined at various temperatures are shown in Figure. 4.15 a) – f). All samples have the hexagonal crystal and similar particle sizes. For the sample calcined above 1050 ^{o}C, the particle size is not much different in theirs size of which in the range of 211.17-224.46 nm.

a) 950 °C
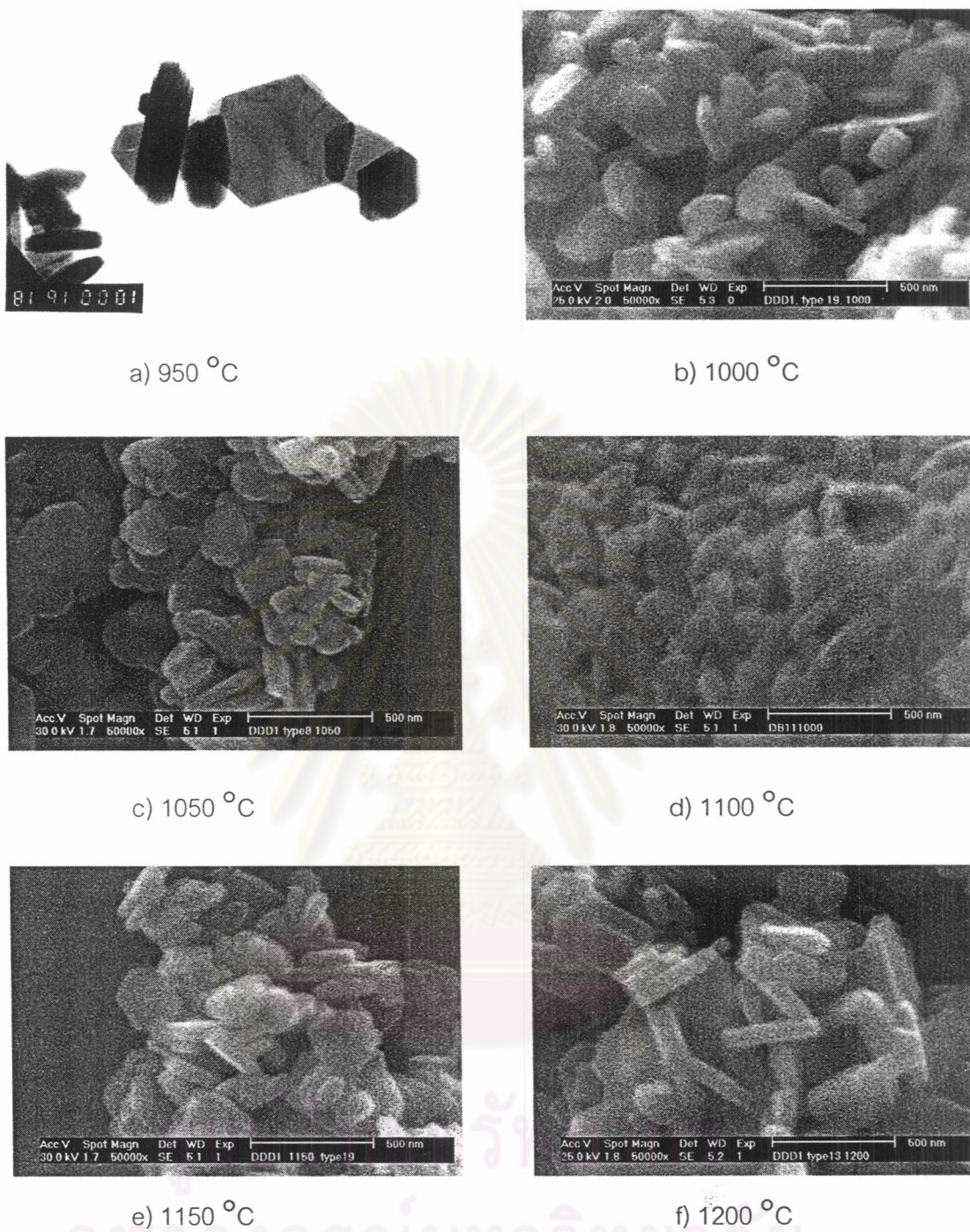
b) 1000 °C

c) 1050 °C

d) 1100 °C

e) 1150 °C

f) 1200 °C

Figure 4.15 Micrographs of the samples nominal dopant level of x = 1.00 soaked for 4
hours at various calcination temperatures a) 950 °C (TEM, 150,000X), b)
1000 °C, c) 1050 °C, d) 1100 °C, e) 1150 °C and f) 1200 °C, (SEM, b-e,
50,000X)

4.2 Effect of calcination temperature on magnetic properties

The values of many magnetic properties can be obtained by a visual analysis of the hysteresis loops (see Chapter 2). Among these properties are the saturation magnetization M_s, the remanent magnetization M_r, and the coercivity H_c. In Tables 4.21 and 4.22, we list the values of these properties of the undoped and doped M-type hexagonal ferrite, respectively. In this part of the study, only the amounts of Sn and Co in the samples were varied.

Table 4.21 Magnetic properties of the undoped M-type type ferrite soaked for 4 hours at
various calcination temperatures

Nominal composition	Temperature (^{o}C)	M_s (emu/g)	M_r (emu/g)	H_c (Oe)
	950^oC	57.48	30.00	5122
	1000^oC	75.24	38.71	5291
$BaFe_{12}O_{19}$	1100^oC	75.29	38.58	5145
	1150^oC	76.30	39.24	4592
	1200^oC	62.34	33.28	3965

Table 4.22 Magnetic properties of the different nominal x level soaked for 4 hours at
various cacination temperatures

Condition	Relative chemical formula	M_s (emu/g)	M_r (emu/g)	H_c (Oe)
a) 950^oC				
x = 0.25	$BaFe_{10.21}Sn_{0.12}Co_{0.45}O_{17.01}$	68.71	35.16	2746
x = 0.50	$BaFe_{10.86}Sn_{0.50}Co_{0.45}O_{18.74}$	56.72	27.42	1706
x = 0.75	$BaFe_{10.34}Sn_{0.64}Co_{0.68}O_{18.47}$	55.85	22.27	895
x = 1	$BaFe_{9.58}Sn_{0.93}Co_{0.86}O_{18.10}$	46.44	20.35	821

Table 4.22(continued) Magnetic properties of the different nominal x level soaked for 4

hours at various cacination temperatures

Condition	Relaitve chemical formula	M_s (emu/g)	M_r (emu/g)	H_c (Oe)
b) $1000^{\circ}C$				
x = 0.25	$BaFe_{10.27}Sn_{0.11}Co_{0.44}O_{17.08}$	68.92	33.44	2686
x = 0.50	$BaFe_{11.45}Sn_{0.50}Co_{0.45}O_{19.54}$	62.02	40.15	2002
x = 0.75	$BaFe_{10.46}Sn_{0.62}Co_{0.67}O_{18.61}$	84.25	35.93	1012
x = 1.00	$BaFe_{9.62}Sn_{0.93}Co_{0.85}O_{18.14}$	41.20	12.77	382
c) $1050^{\circ}C$				
x = 0.25	$BaFe_{10.39}Sn_{0.11}Co_{0.44}O_{17.25}$	67.19	33.05	2136
x = 0.50	$BaFe_{11.17}Sn_{0.47}Co_{0.46}O_{19.14}$	78.82	38.20	1965
x = 0.75	$BaFe_{10.25}Sn_{0.64}Co_{0.65}O_{18.32}$	69.81	30.31	1141
x = 1.00	$BaFe_{9.78}Sn_{0.83}Co_{0.86}O_{18.29}$	40.26	11.16	409
d) $1100^{\circ}C$				
x = 0.25	$BaFe_{10.71}Sn_{0.12}Co_{0.45}O_{17.76}$	69.00	31.72	1458
x = 0.50	$BaFe_{11.39}Sn_{0.45}Co_{0.46}O_{19.45}$	76.30	36.58	2050
x = 0.75	$BaFe_{10.29}Sn_{0.64}Co_{0.65}O_{18.36}$	69.81	29.67	1092
x = 1.00	$BaFe_{10.16}Sn_{0.88}Co_{0.91}O_{18.93}$	45.38	11.37	291
e) $1150^{\circ}C$				
x = 0.25	$BaFe_{10.47}Sn_{0.11}Co_{0.44}O_{17.37}$	76.95	32.34	1091
x = 0.50	$BaFe_{11.14}Sn_{0.45}Co_{0.45}O_{19.06}$	76.72	35.89	1912
x = 0.75	$BaFe_{10.25}Sn_{0.65}Co_{0.64}O_{18.24}$	68.47	26.54	866
x = 1.00	$BaFe_{9.52}Sn_{0.95}Co_{0.84}O_{18.02}$	45.08	9.31	281
f) $1200^{\circ}C$				
x = 0.25	$BaFe_{10.47}Sn_{0.11}Co_{0.44}O_{17.37}$	79.21	34.78	1049
x = 0.50	$BaFe_{11.14}Sn_{0.45}Co_{0.45}O_{19.06}$	81.73	36.78	1420
x = 0.75	$BaFe_{10.25}Sn_{0.65}Co_{0.64}O_{18.24}$	70.29	14.81	432
x = 1.00	$BaFe_{9.52}Sn_{0.95}Co_{0.84}O_{18.02}$	40.73	7.71	231

4.2.1. Saturation magnetization

Table 4.21 shows that the saturation magnetization of the undoped ferrites calcined at different temperatures are in the range between 57.48-76.30 emu/g. We see that saturation magnetization increases when the calcination temperatures is increased up to 1150° C where it has its highest value. It then becomes smaller when the calcination temperature is raised to 1200°C. The increase in the saturation magnetization when the calcination temperature is raised can be attributed to the improved purity and crystallinity of the $BaFe_{12}O_{19}$, specimens as determined from the x-ray data. As reported by Henada et al. the M_s of their pure $BaFe_{12}O_{19}$ increased from 55 to 63 emu/g when the annealing temperature was increased from 800 to 1100°C. The similar result was reported by Wang et al (1995). In the Figure 4.16, we see that the M_s of the doped sample having nominal dopant levels of x= 0.25-1.00. The change in M_s of the nominal x = 0.25 and 0.50 occurring when the calcination temperatures is increased can be explained by the increasing substitution of the dopants into the $4f_{iv}$ sites. From equation 2.16, the substitution of the dopants into the $4f_{iv}$ sites causes the decrease of spin up moment, so the total moment decreases. This leads to the decrease in the saturation magnetization. The change of saturation magnetization with temperature in the other samples can be explained by the same way.
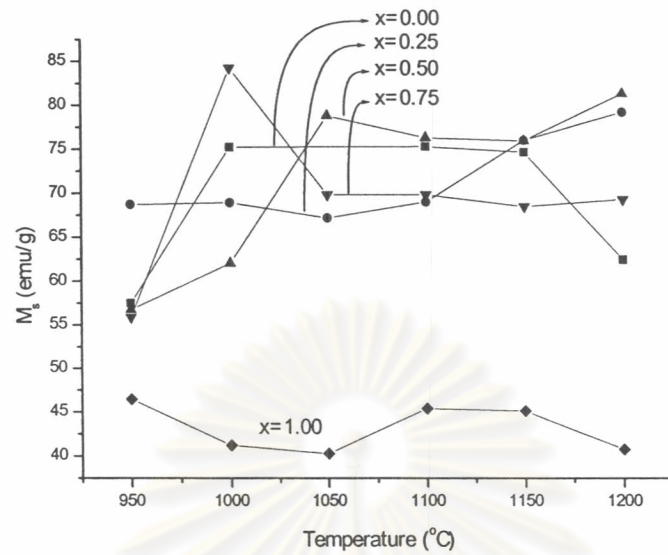
Figure 4.16 Effect of the calcination temperatures on M_s (emu/g) for various dopant level between x=0.00 - 1.00

4.2.2. Remanant magnetization

The remanant magnetization of specimens calcined at different temperatures are given in Table 4.22 and shown in Figure 4.17. As can be seen, all the curves of M_r reach a turning point at 1000°C. The remanent magnetization of the nominal doping x levels of 0.25 and 0.50 specimens increase as the calcination temperature is raised. However, the remanent magnetization of the other doped ferrites decreases as the calcination temperature is increased.
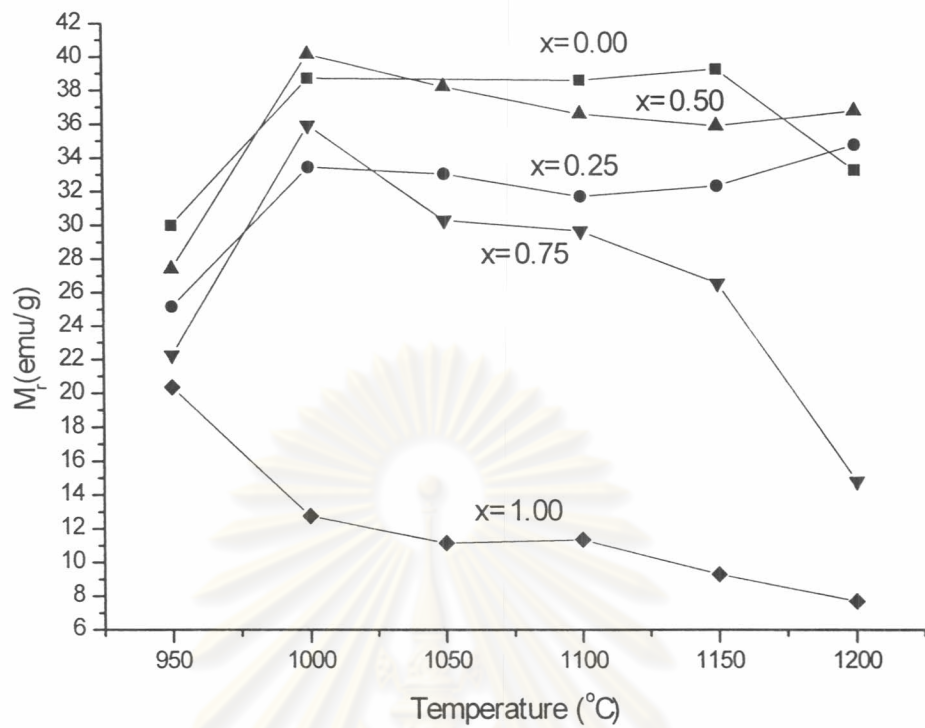
Figure 4.17 The dependence of M_r on the calcination temperature of the doped BaF when the nominal dopant levels between 0.00 and 1.00

4.2.3. Coercivity

Table 4.22 and Figure 4.18 show that the substitution of Co and Sn into the BaF leads to decreases in the coercivity of most samples. Ram et al., attributed the decrease to an increase in the stress within the crystal when Bi^{3+} ions were substituted into the structure. Gonzalez-Angeles et al. (2004), attributed the decreases to the decrease in the uniaxial crystalline anisotropy resulting when the tetravalent ions replace the Fe^{3+} located on the 4e (2k site) in the magnetoplumbite structure.
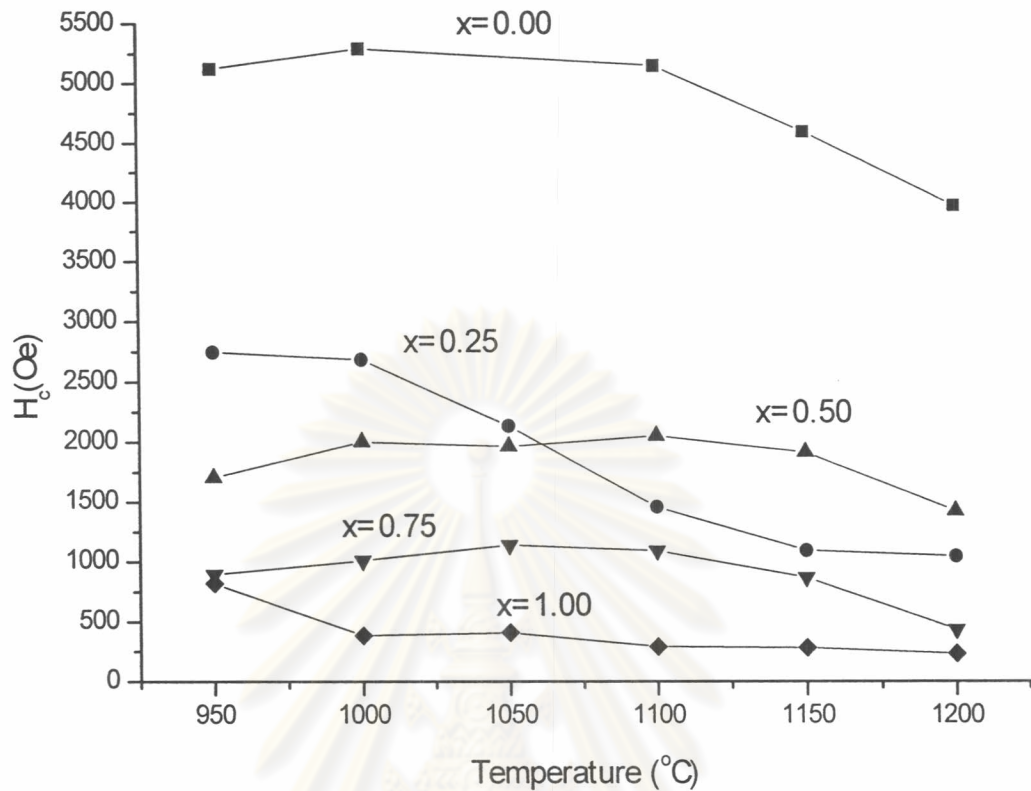
Figure 4.18 Temperature dependence of H_c for doping at levels between 0.00 and 1.00

From Figure 4.19, It is seen that the H_c increases as the surface area to volume ratios (S/V) also increases.
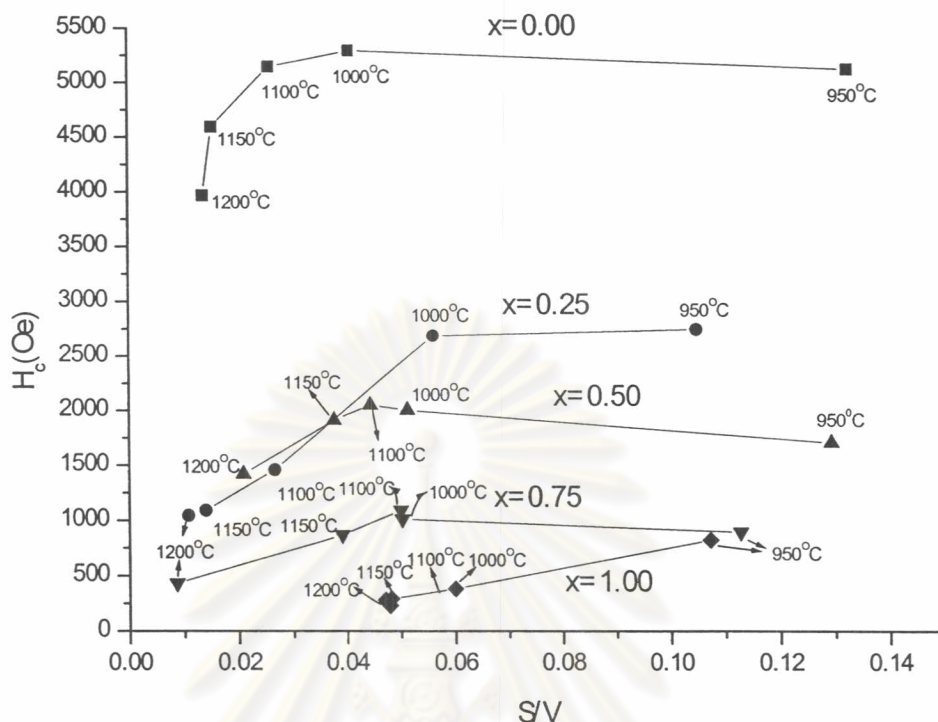
Figure 4.19 The dependence of H_c on the surface area to volume ratio of sample soaked

for 4 hours at various cacination temperature when nominal x=0.00 -1.00

4.2.4   The relation of particle size and saturation magnetization

In Table 4.23 show the relation between particle size and saturation magnetization of undoped and doped M-type hexaferrite. We do not see any systematic change of grain size and saturation magnetization in undoped samples and doped samples. Generally, the magnetization depends on the amount of moment in samples. However, the saturation magnetization of the nominally x=0.25 doped BaF increase with increase the particle size for temperature above 1050 $^\circ$C. This may be due to the crystallization effect more than the effect of grain size. The maximum saturation magnetization seen 84.25 emu/g in the sample of the nominally x=0.75 doped BaF.

Table 4.23 The relation of particle size and saturation magnetization

Nominal x	T (°C)	D (nm)	Ms (emu/g
0.00	950	88.33	57.48
	1000	216.65	75.24
	1100	312.89	75.29
	1150	485.55	76.30
	1200	881.39	62.43
0.25	950	99.50	68.71
	1000	163.41	68.92
	1050	237.41	67.19
	1100	334.85	69.00
	1150	682.47	76.95
	1200	956.27	79.21
0.50	950	117.50	56.72
	1000	191.70	62.02
	1050	279.64	78.82
	1100	237.29	76.30
	1150	337.46	76.72
	1200	481.06	81.73
0.75	950	112.50	55.85
	1000	215.77	84.25
	1050	217.91	69.81
	1100	222.81	69.81
	1150	268.46	68.47
	1200	945.29	70.29
1.00	950	90.00	46.44
	1000	166.73	41.20
	1050	206.79	40.26
	1100	211.17	45.38
	1150	213.18	45.08
	1200	224.46	40.73

4.3   Mossbauer measurement

The mossbauer spectroscopy is used to determine the internal magnetic field of ordered magnetic materials. We have selected the codoped barium hexaferrites which were calcined at 1000°C for 4 hours to study by the Mossauer spectrometer. The reason for choosing this series is that their coercivity appear to change systematically but that their saturation magnetization does not. The Mossbauer measurements might tell why. The values of many parameters in the Mossbauer spectrums are given in Table 4.23. It can be seen that for the undoped sample, there is no hyperfine field having a value of 402 kOe. If the Fe^{3+} ions enter in sufficient numbers into the 12k sites and form into a sublattice, one would expect a hyperfine field of this strength to appear in the spectrum. This implies that either the lattice containing the 12k sites did not form at a calcination temperature of 1000 $^{\circ}$C or there is a greater deal of disorder (in the arrangement of the Fe^{3+} ions among the different lattice sites) present in the crystal structure. It should be noted that the XRD patterns for these BaF specimen shows that the crystal structure has formed. Supporting this view, we note that a dopant of x = 0.25 produces a ferrite having hyperfine field of 407.1 kOe. Since the addition of sintering aids lowers the required calcination temperature which would be equivalent to raising the calcination temperature, a more ordered crystal structure would occur. Also, the grain size would get larger. This would enhance the interactions that give rise to the hyperfine field.

Table 4.24 Mossbauer spectrum of specimens containing nominal Co/Sn dopant levels between 0.00 and 1.00 which were calcined for 4 hours at $1000^{\circ}C$

Chemical formula	Mossbauer parameter				
	H_{hpf} (koe)	Δ (mm/s)	IS (mm/s)	Γ (mm/s)	Area (%)
X = 0	363	1.670	0.200	0.051	47.36
	459	0.096	0.171	0.234	33.30
	407	0.231	0.435	0.420	4.77
	342	0.250	0.202	1.76	7.30
	402	0.240	0.210	0.237	7.17
	-	0.181	0.070	0.905	<0.1
X = 0.25 ($BaFe_{10.27}Sn_{0.11}Co_{0.44}O_{17.06}$)	407	1.792	0.177	0.289	52.72
	461	0.274	0.269	-0.308	11.87
	480	0.338	0.128	0.165	15.41
	395	0.218	-0.287	1.231	8.26
	405	0.283	0.192	0.256	11.74
X = 0.50 ($BaFe_{11.45}Sn_{0.46}Co_{0.45}O_{19.54}$)	384	1.668	0.22	0.845	69.1
	461	0.511	0.193	-0.011	17.78
	443	0.267	-0.048	0.250	6.94
	345	0.278	0.237	1.772	6.11
	-	0.125	0.074	0.906	<1
X = 0.75 ($BaFe_{1.46}Sn_{0.62}Co_{0.62}O_{18.61}$)	365	1.721	0.246	0.772	75.890
	445	0.377	0.184	0.029	14.318
	427	0.307	0.193	-0.100	8.23
	337	0.262	0.353	1.583	7.24
	-	0.224	0.659	1.694	1.5
X = 1.00 ($BaFe_{9.62}Sn_{0.93}Co_{0.85}O_{18.14}$)	365	1.721	0.246	0.077	68.8
	445	0.377	0.184	0.029	14.32
	427	0.307	0.193	-0.100	8.23
	336	0.262	0.353	1.583	7.24
	-	0.224	0.659	1.694	1.5