Chapter V

Results and Discussion

5.1 Formation of pure zinc gallate

The reaction of gallium acetylacetonate and zinc acetate (molar ratio Zn/Ga=0.5)in the glycol and alcohol organic solvent (1,4-butanediol, 2-propanol, and 1-butanol) at 300°C under autogeneous pressure yielded nanocrystalline zinc gallate. The XRD patterns of the products obtained by all the reactions show that spinel phase was directly crystallized. Both of the crystallite size and the BET surface area of zinc gallate depend on the type of organic solvents.

5.1.1 Reaction in 1,4-butanediol (Glycothermal reaction)

The XRD patterns of the as-synthesized products with various Zn/Ga molar ratios in the starting mixture obtained from glycothermal reaction at 300°C for 2 h are given in Figure 5.1, which shows that spinel phase was formed without contamination with other phases such as ZnO and Ga_2O_3 at the starting molar ratio Zn/Ga = 0.5 (stoichiometric ratio). However, at starting Zn/Ga molar ratio equal to 0.33 and 1.00 shown the peaks of contaminate phase of gallium oxide and zinc oxide, respectively. The crystallite size of the product at various starting Zn/Ga molar ratios calculated by XRD broadening using Scherer equation was between 10.86 and 14.42 nm. The average particle sizes determined by using transmission electron micrograph (TEM) of them were between 10.3 and 14.67 nm, which is in good agreement with the crystallite sizes. Then, they indicated that each primary particle observed by TEM is a single crystal of spinel zinc gallate. The BET surface area of these products at starting Zn/Ga equal to 0.33, 0.50 and 1.00 were 76.51, 52.27, and 67.69 $m^2 g^{-1}$, respectively (Table 5.1).

The product was calcined at temperature of 600 to 1100°C. The BET surface area and XRD patterns of the calcined products were investigated. BET surface area and crystallite sizes of the products at various starting Zn/Ga molar ratios after calcination at 600°C, 800°C, and 1100°C were m^2g^{-1}(Table 5.1). Their XRD patterns were almost identical to that before calcination except the fact that the peaks were more sharp (Figure 5.2 to 5.4). As expected from this pattern, these products still preserved the spinel structure even after calcination at 1100°C.

The crystallite sizes of the products which calculated by the XRD broadening are shown in Table5.1. Figure 5.5(a) to 5.5(f) shows TEM photographs of the products at various starting Zn/Ga molar ratios before and after calcination at 1100°C.

5.1.2 Reaction in toluene (Thermal decompostion reaction)

Thermal decompostions of gallium acetyl acetonate in toluene at 300°C for 2h did not occur because of the gallium acetyl acetonate is more stable. Thus, solid product was not obtained. It shows that the spinel product was not formed.

5.1.3 Reaction in 2-propanol (Transfer hydrolytic crystallization in alcohols reaction, THyCA)

The as-synthsized products of zinc gallate obtained by the reaction in 2-propanol had the crystallite sizes between and 8.and nm calculated by using Scherer equation .The XRD patterns of the as-synthesized products at various starting Zn/Ga molar ratios are shown in Figure5.6. TEM photographs of as-synthesized products at various starting Zn/Ga molar ratios and solvents are shown in Figure5.10(a), (c) and (e). These results are good agreement with the crystallite sizes that observed by XRD broadening technique. Then it can be indicated that the product is a single crystal of spinel. The XRD patterns of the products at various starting Zn/Ga ratios before and after calcination at various temperatures are shown in Figure 5.7 to 5.9. In Figure 5.10

(a) to (f), TEM photographs of the products before and after calcination at 1100C° are shown.

The BET surface areas of as-synthesized products prepared in 2-propanol were , 79.63, and 85.97 m^2g^{-1}at starting Zn/Ga equal to 0.33, 0.50 and 1.00, respectively (Table5.2). The specific surface areas and the crystallite sizes of the products at various starting Zn/Ga molar ratios and solvents after calcination at 600, 800, and 1100°C are shown in Table 5.2.

5.1.4 Reaction in 1-butanol

The BET surface areas of as-synthesized products prepared in 1-butanol were , 79.63, and 85.97 m^2g^{-1}at starting Zn/Ga equal to 0.33, 0.50 and 1.00, respectively (Table5.2). The specific surface areas and the crystallite sizes of the products at various starting Zn/Ga molar ratios and solvents after calcination at 600, 800, and 1100°C are shown in Table 5.3. The XRD patterns of the products at various starting Zn/Ga ratios are shown in Figure 5.11. The XRD patterns of them before and after calcination at various temperatures are shown in Figure 5.12 to 5.14. And TEM photographs of the products before and after calcination at 1100°C are shown in Figure 5.15 (a) to (f).

5.2 Formation of pure zinc aluminate

Similarly, the reaction of aluminium isopropoxide and zinc acetate with the same molar ratio as preparing zinc gallate in each of the organic solvent yielded nanocrystalline zinc aluminate. And, the reaction of them in toluene could occur yielding the solid products.

5.2.1 Reaction in 1,4-butanediol (glycothermal)

The XRD patterns of the as-synthesized product obtained from glycothermal reaction at 300°C for 2 h with various ratios of Zn/Al in the starting mixture are

shown in Figure 5.16. It has been found that the sample with Zn/Al ratios of 0.50 exhibited the completely similar XRD characteristic peaks to the spinel phase. As for the samples with higher Zn/Al ratio(1.00) another peaks were observed which should be ascribed to the prescence of an excess amount of ZnO and smaller Zn/Al ratio (0.33) another peaks were observed which should be ascribed to the prescence of an excess amount of Al_2O_3. These may cause less uniformity of the samples obtained compared with stochiometric ratio sample. The crystallite sizes, which calculated by the XRD brodening of the products at starting Zn/Al ratio 1.00, 0.50 and 0.33 were 7.9, 9.8 and 12.4 nm, respectively. The average particle sizes determined from the transmission electron micrographs (TEM) of the samples (Figure 5.20(a), (c), (e)) were 7.67, 9.33, and 12.33 nm, which is in good agreement with the crystallite sizes, indicating that each primary particle observed by TEM is a single crystal of spinel. The BET surface area of the products at starting Zn/Al ratio 1.00, 0.50 and 0.33 were 86.7, 155.68 and 156.35 m^2g^{-1}, respectively.

The product was calcined at temperature of 600, 800, and 1100°C. The BET surface area and the XRD pattterns of the calcined products were investigated. The BET surface area of the products after calcination at various temperature were shown in Table5.4 . The XRD patterns were almost indentical to that before calcination except that the peaks were more sharp (Figure 5.17 to 5.19). As expected from the pattern of the products at starting Zn/Al = 0.50, the product still preserved the spinel structure even after calcination at 1100°C.

5.2.2 Reaction in toluene (Thermal decomposition reaction)

The thermal decompositions of zinc acetate and aluminum isopropoxide in toluene at the same condition yielded nanocrystalline zinc aluminate powders. The XRD patterns of the as-synthesized products are given in Figure 5.21. It shows that at Zn/Al = 0.5, spinel phase was formed without another phase of zinc oxide and alumina, which was similar to that prepared in 1,4-butanediol. TEM photographs of as-synthesized products at various starting Zn/Al molar ratios are shown in Figure 5.25(a), (c), and (e). The particle sizes of the products observed by TEM photographs

are in good agreement with the crystallite sizes determined by XRD line broadening technique. This suggests that each particle observed by TEM is a single crystal of spinel. And in Figure 5.22 to 5.24, the XRD patterns of the products before and after calcination at various temperatures are shown.

The as-synthesized products were prepared by this method had a large surface area and after calcination at 600°C and 800°C were decreased. After calcination at 1100°C, BET surface area drastically decreased as shown in Table 5.5.

5.2.3 Reaction in 2-propanol

The crystallite sizes of the as-synthesized products obtained by 2-propanol at starting Zn/Al 1.00, 0.50 and 0.33 were 9.7, 10.43, and 9.75 nm, which is calculated by XRD broadening technique. The XRD patterns of the as-synthesized products at various starting Zn/Al ratios were shown in Figure5.26. The average particle sizes determined from TEM photographs of as-synthesized products as shown in Figure5.30 (a), (c), and (e). These results show good agreement with the crystallite sizes that observed by XRD broadening technique. Then it can be indicated that the product is a single crystal. In Figure 5.27 to 5.29, the XRD patterns of the products before and after calcination at various temperatures are shown.

The BET surface area of the as-synthesized products prepared in 2-propanol and calcined products were shown in Table 5.6.

5.2.4 Reaction in 1-butanol

The crystallite sizes calculated by XRD broadening technique of the as-synthesized products obtained by 1-butanol and the products after calcination at various temperature are shown in Table 5.7 . TEM photographs of the products before and after calcination at 1100° are shown in Figure 5.35 (a) to (f). These results shows good agreement with the crystallite sizes that observed by XRD broadening

technique. Then it can be indicated that the product is a single crystal. And the XRD patterns of the as-synthesized products and the calcined products were shown in Figure 5.32 to 5.34.

The BET surface area of as-synthesized products prepared in 1-butanol and the calcined products were shown in Table5.7. The chemical composition of zinc gallate and zinc aluminate products was shown in Table 5.8.

As described above, it was found that BET surface area of zinc gallate and zinc aluminate synthesized by solvothermal method was larger than that synthesized by other methods. Tables 5.9 shown the BET surface area of the zinc gallate and zinc aluminate synthesized by various methods.

Table 5.9 BET surface area of prepared samples.

Sample	BET surface area (m^2/g)
Coprecipitated $ZnAl_2O_4$	20
Sol-gel $ZnAl_2O_4$	50
Wet mixing $ZnAl_2O_4$	22
Solvothermal $ZnAl_2O_4$	
in 1,4-butanediol	155.68
toluene	197.11
2-propanol	80.94
1-butanol	139.51
Coprecipitated $ZnGa_2O_4$	26
Solvothermal $ZnGa_2O_4$	
in 1,4-butanediol	52.27
2-propanol	79.63
1-butanol	113.42

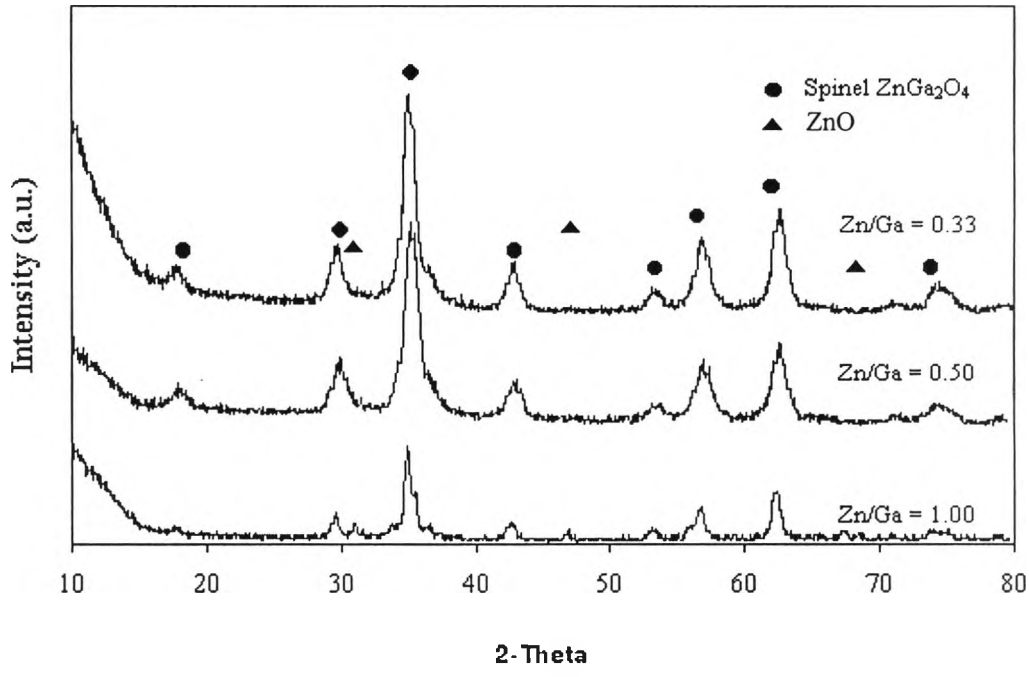

Figure 5.1 The XRD patterns of zinc gallate products at various starting Zn/Ga ratios synthesized in 1,4-butanediol.

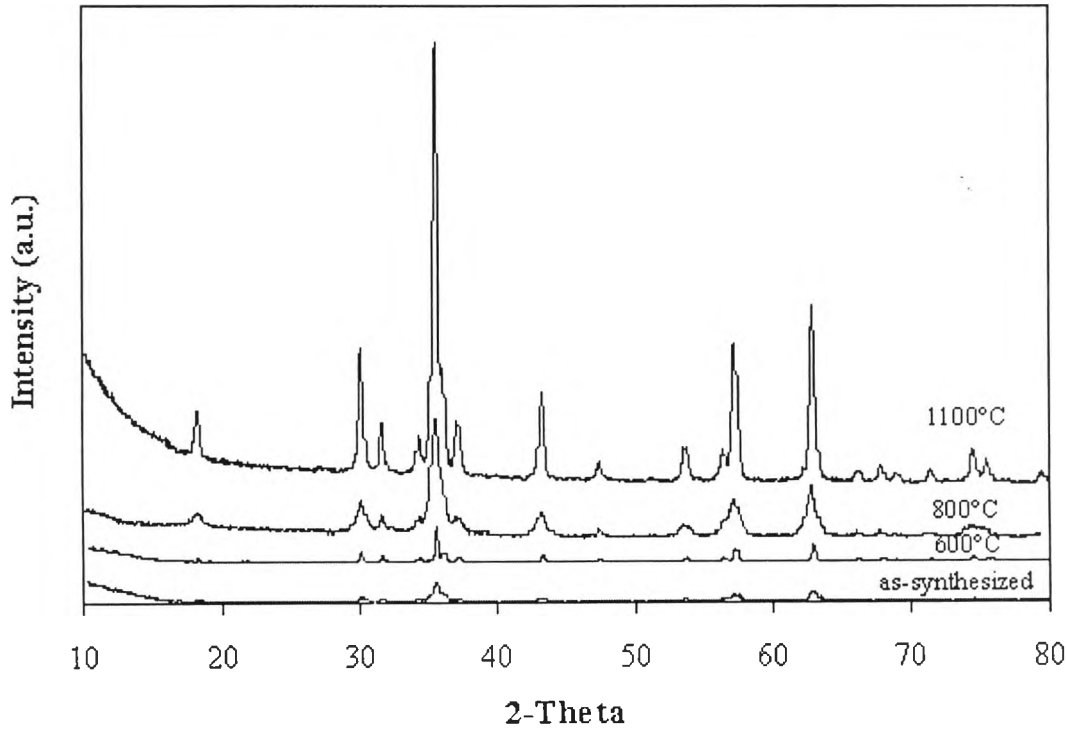

Figure 5.2 The XRD patterns of the products at starting Zn/Ga = 1.00 synthesized in 1,4-butanediol before and after calcination at 600, 800, and 1100°C.

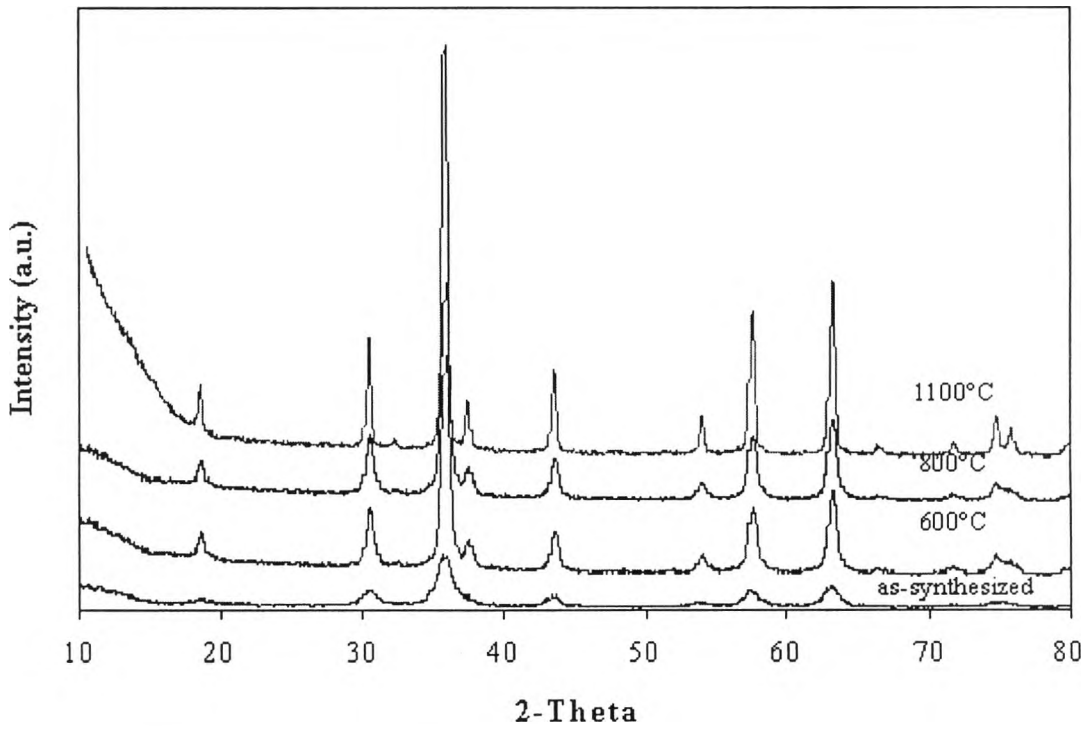

Figure 5.3 The XRD patterns of the products at starting Zn/Ga = 0.50 synthesized in 1,4-butanediol before and after calcination at 600, 800,1100°C.

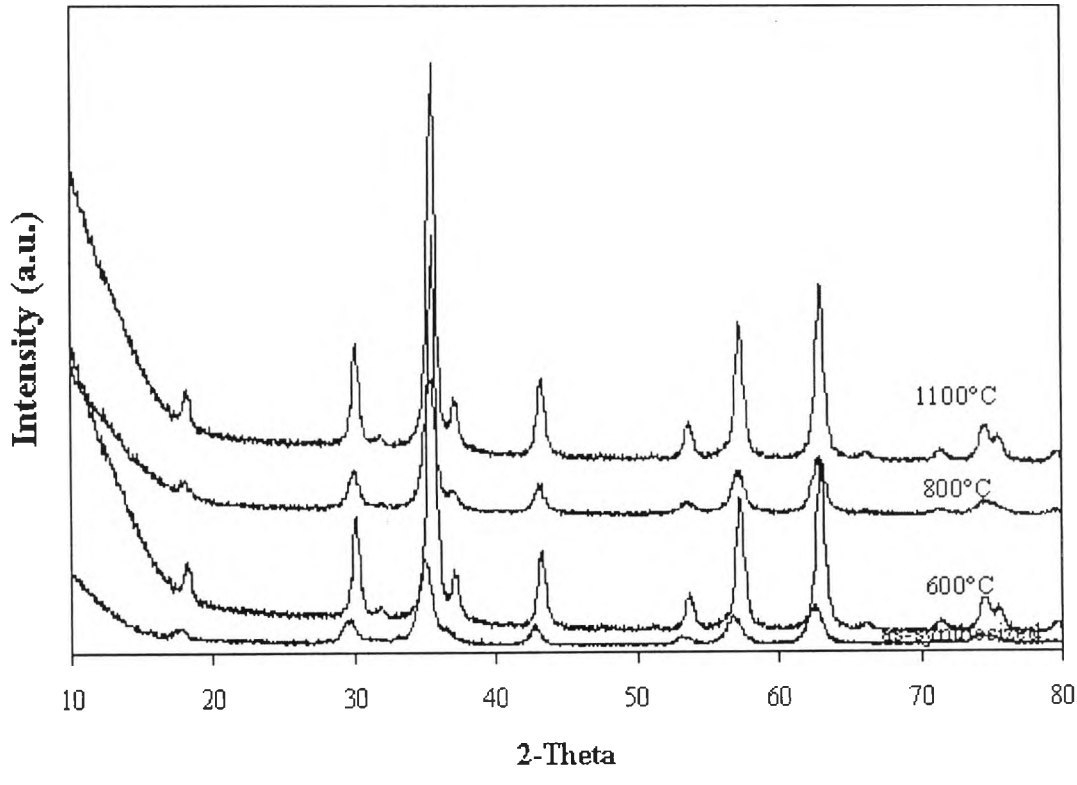

Figure 5.4 The XRD patterns of the products at starting Zn/Ga = 0.33 synthesized in 1,4-butanediol before and after calcination at 600, 800, and 1100°C.

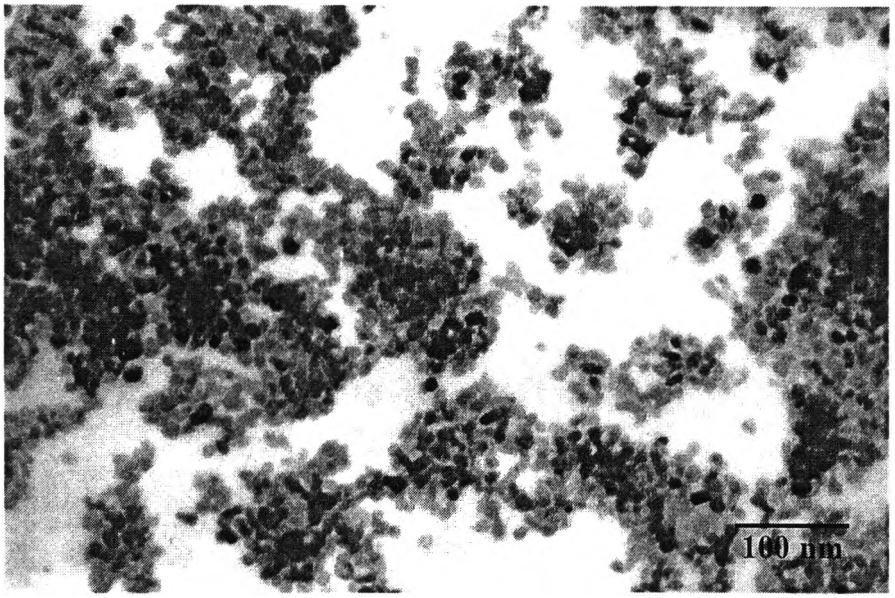

Figure 5.5(a) TEM photograph of the product at Zn/Ga = 1.00 synthesized in 1,4-butanediol .

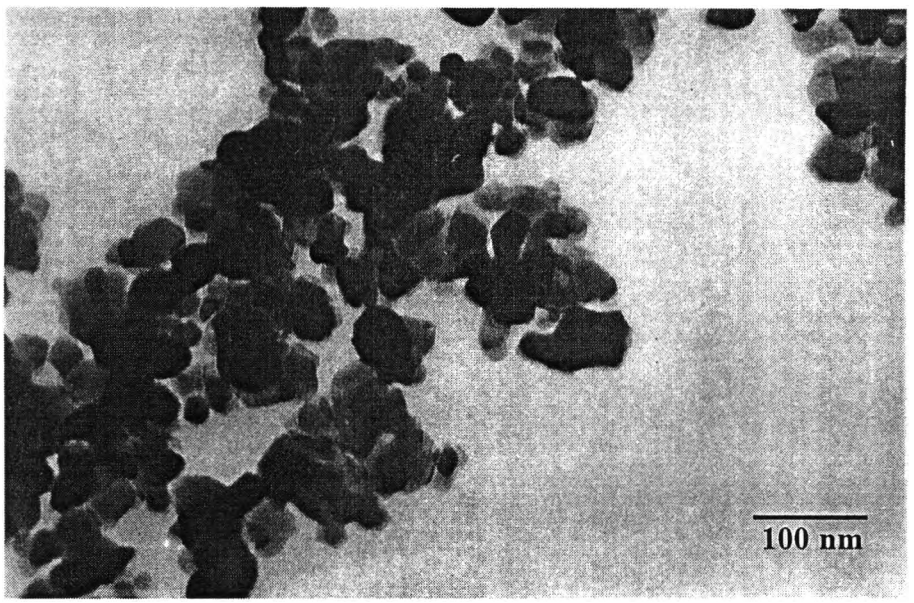

Figure 5.5(b) TEM photograph of the product at staring Zn/Ga = 1.00 synthesized in 1,4-butanediol after calcination at 1100°C.

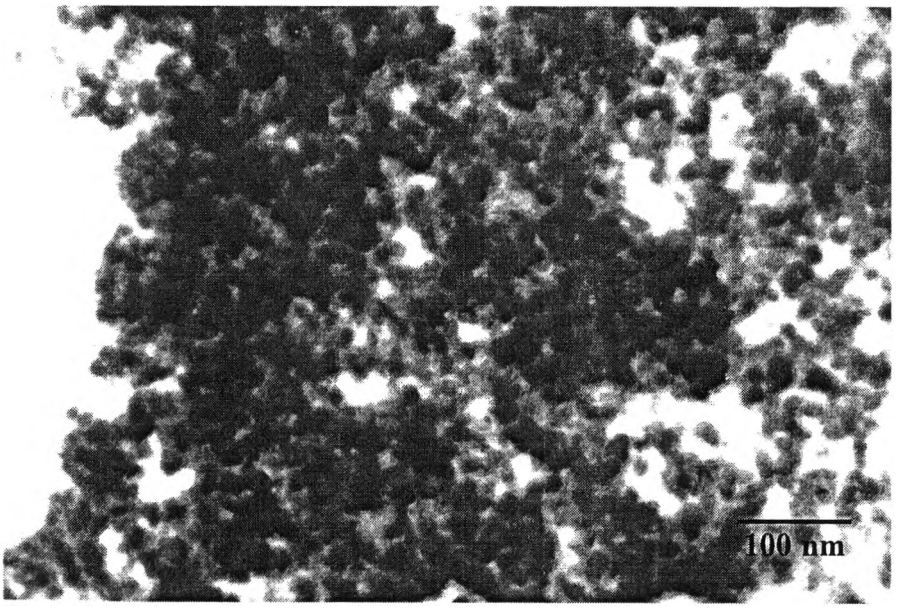

Figure 5.5(c) TEM photograph of the product at starting Zn/Ga = 0.50 synthesized in 1,4-butanediol.

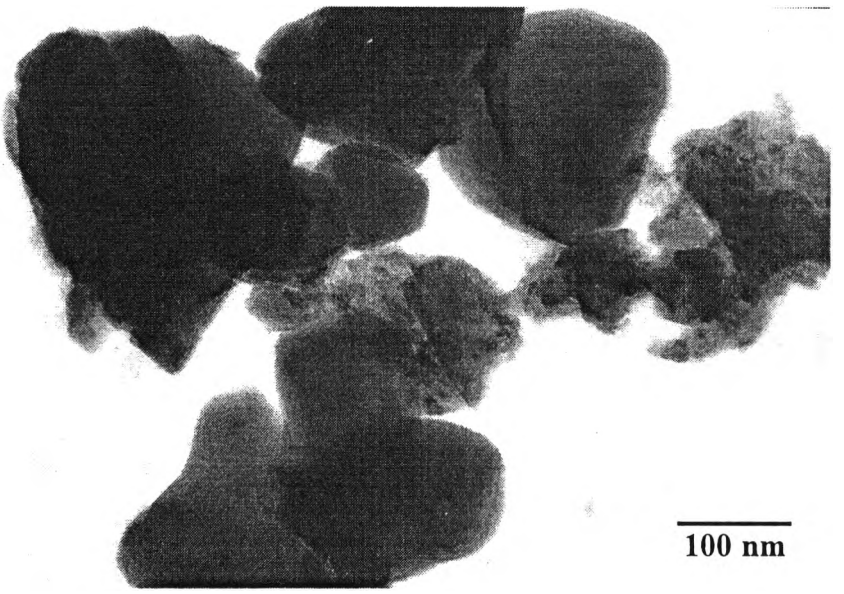

Figure 5.5(d) TEM photograph of the product at starting Zn/Ga = 0.50 synthesized in 1,4-butanediol after calcination at 1100°C.

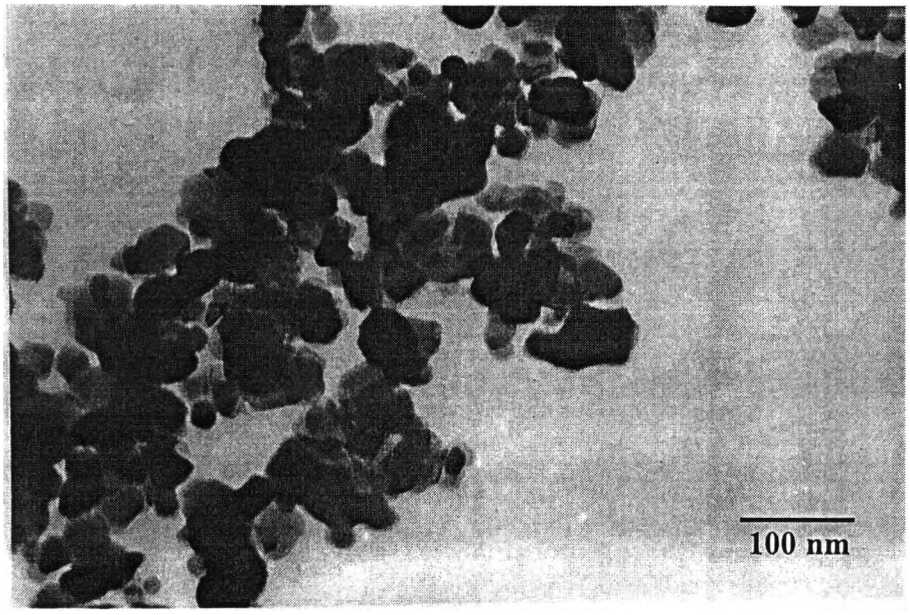

Figure 5.5(e) TEM photograph of the products at starting Zn/Ga = 0.33 synthesized in 1,4-butanediol.

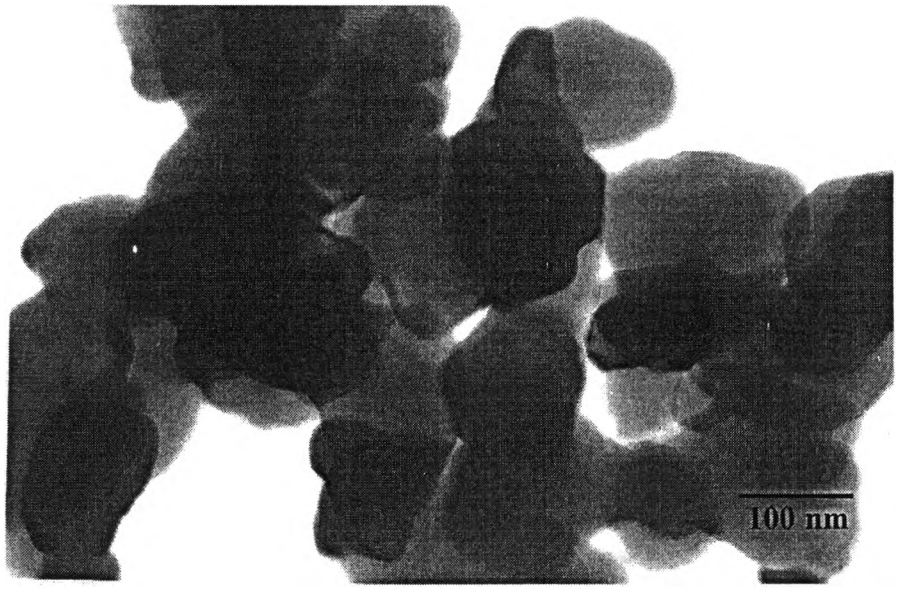

Figure 5.5(f) TEM photograph of the product at starting Zn/Ga = 0.33 synthesized in 1,4-butanediol after calcination at 1100°C.

Table 5.1 BET surface area and crystallite size of the zinc gallate products synthesized by 1,4-butanediol and the samples calcined at various temperatures.

Charged Zn/Ga ratio	S_{BET}[a] (m^2/g)				d[b] (nm)				d[c] (nm)			
	as-syn	600°C	800°C	1100°C	as-syn	600°C	800°C	1100°C	as-syn	600°C	800°C	1100°C
0.33	76.51	54.13	45.81	17.14	10.86	14.21	19.89	40.23	10.67	14.33	19.99	40.33
0.50	52.27	36.59	17.25	11.50	18.13	46.73	66.74	127.54	18.33	46.67	66.33	128.67
1.00	67.69	35.05	17.78	6.57	14.42	27.80	52.17	78.31	14.33	27.67	52.33	78.33

[a]BET surface area.

[b]Crystallite size of the products calculated from Scherer equation using KCl as an internal standard

[c]Crystallite size of the products from TEM photograph.

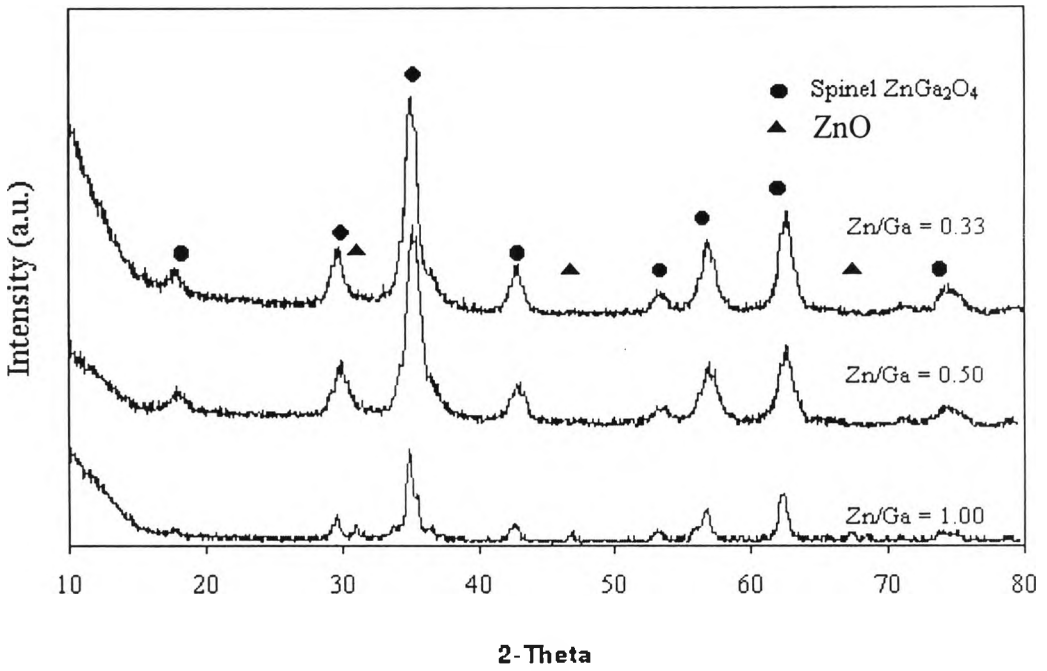

Figure 5.6 The XRD patterns of the zinc gallate products at various starting Zn/Ga synthesized in 2-propanol.

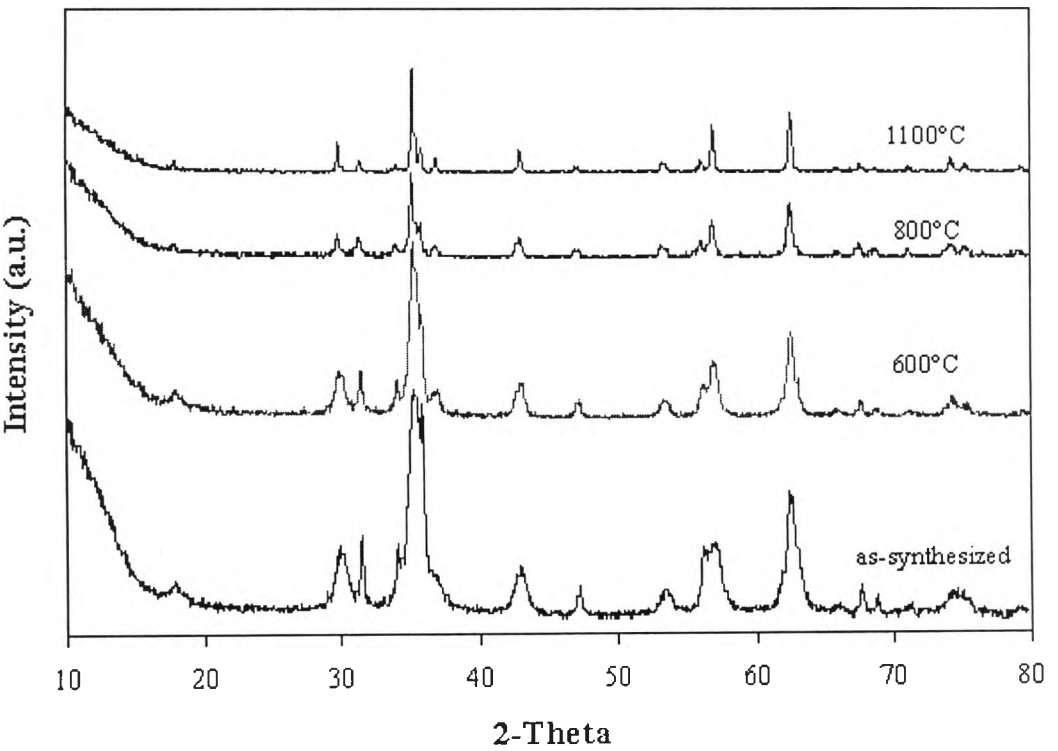

Figure 5.7 The XRD patterns of the products at starting Zn/Ga = 1.00 synthesized in 2-propanol before and after calcination at 600, 800, and 1100°C.

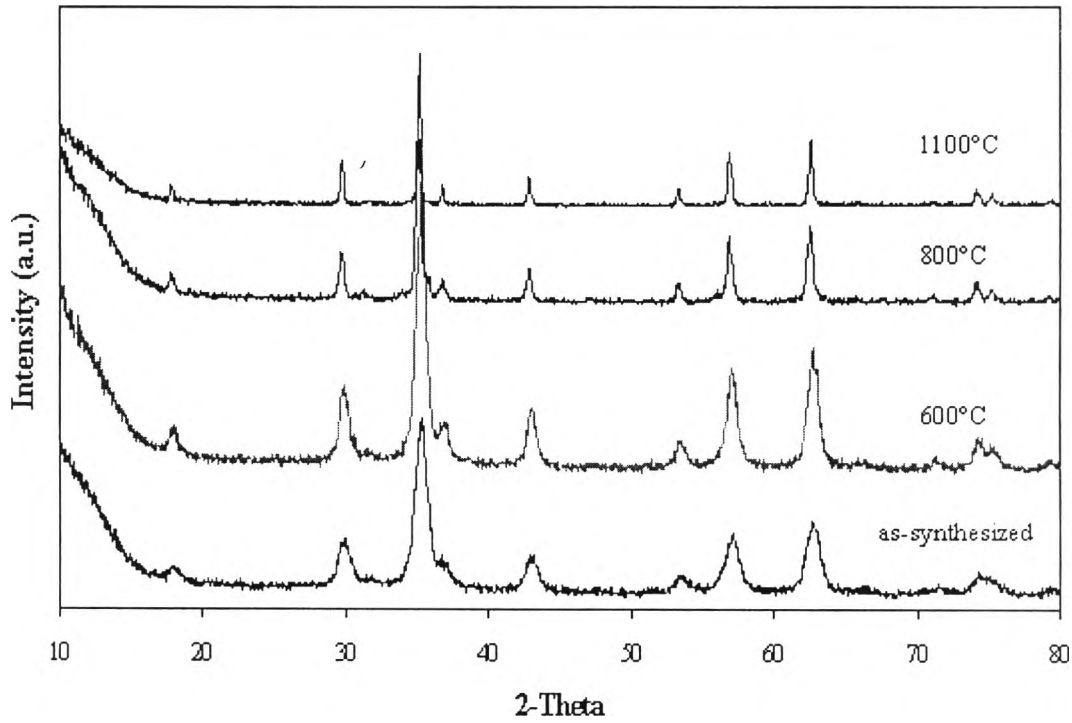

Figure 5.8 The XRD patterns of the products at starting Zn/Ga = 0.50 synthesized in 2-propanol before and after calcination at 600, 800, and 1100°C.

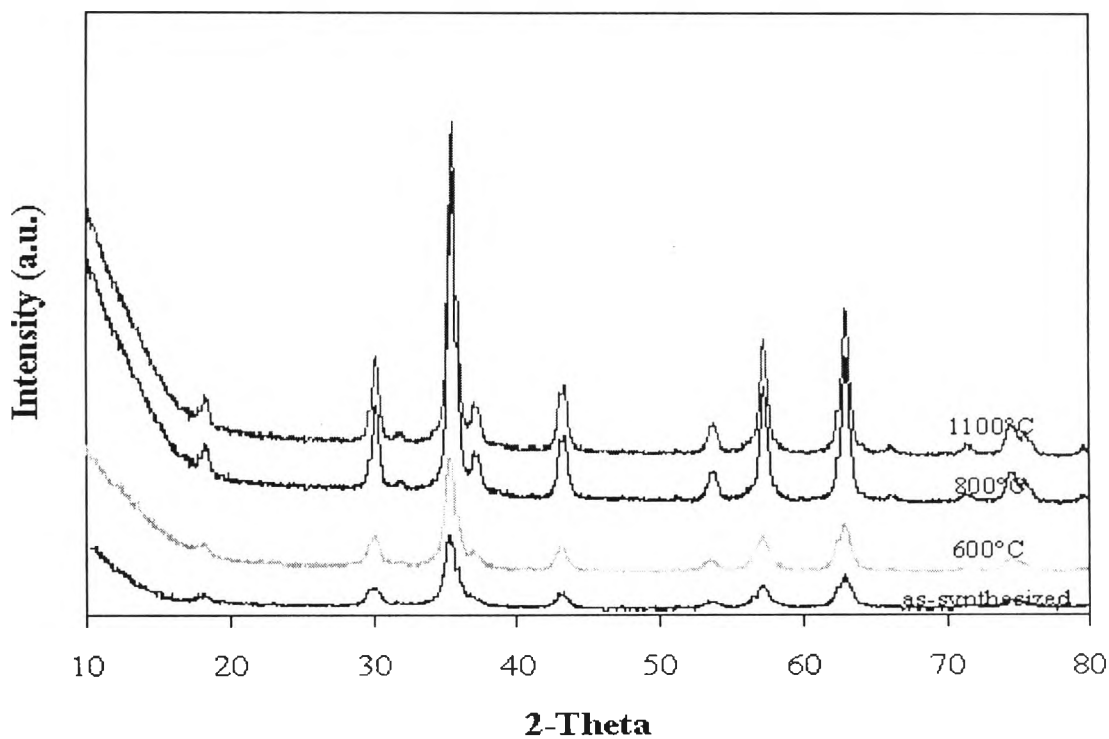

Figure 5.9 The XRD patterns of the products at starting Zn/Ga = 0.33 synthesized in 2-propanol before and after calcination at 600, 800, and 1100°C.

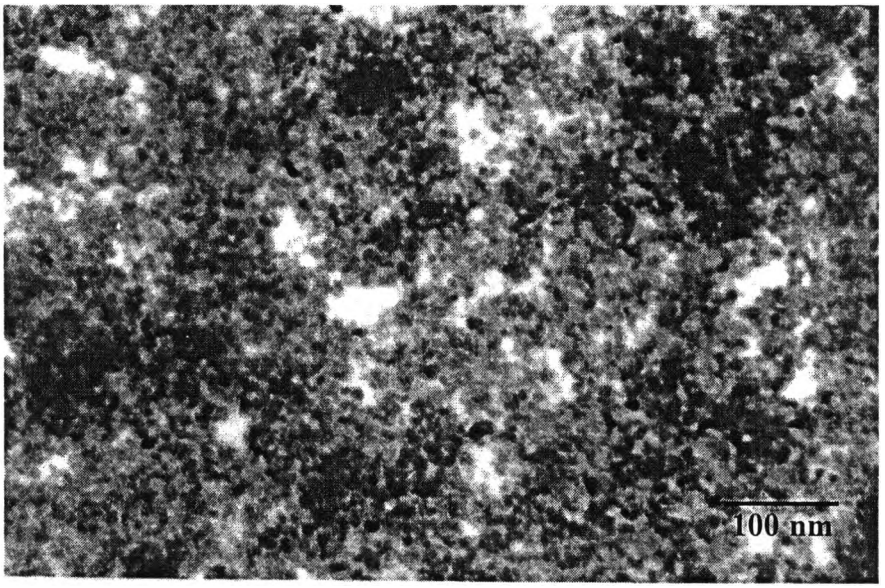

Figure 5.10(a) TEM photograph of the product at staring Zn/Ga = 1.00 synthesized in 2-propanol.

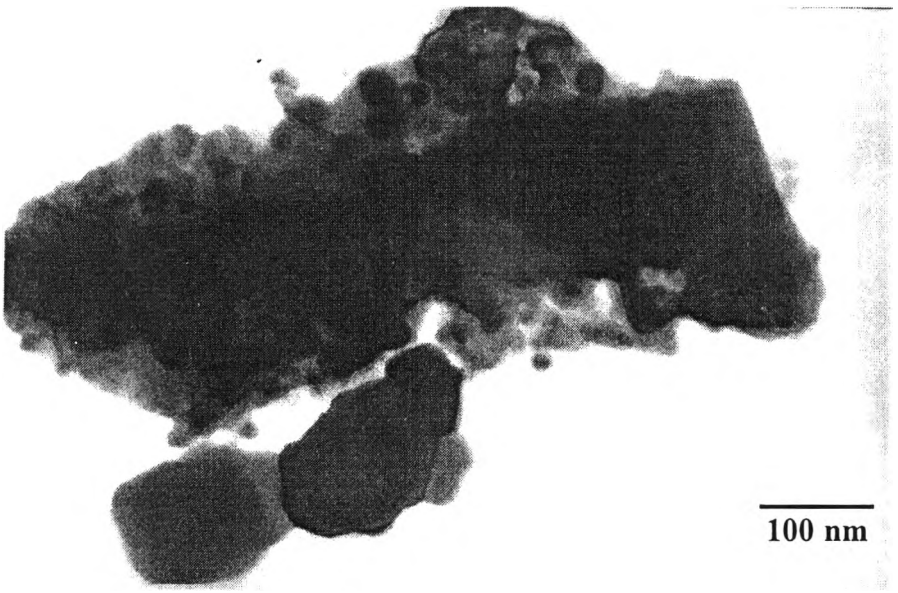

Figure 5.10(b) TEM photograph of the product at starting Zn/Ga = 1.00 synhthesized in 2-propanol after calcination at 1100°C.

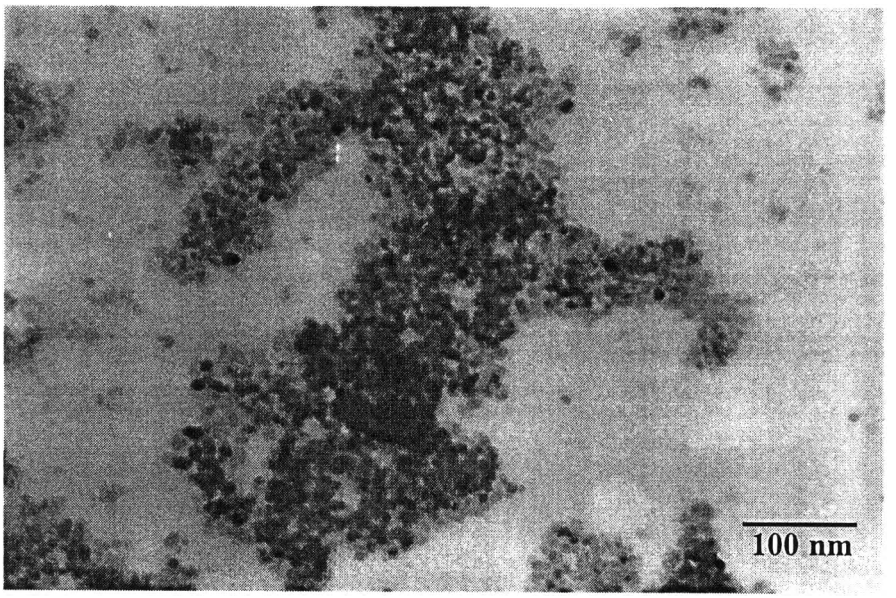

Figure 5.10(c) TEM photograph of the product at starting Zn/Ga = 0.50 synthesized in 2-propanol.

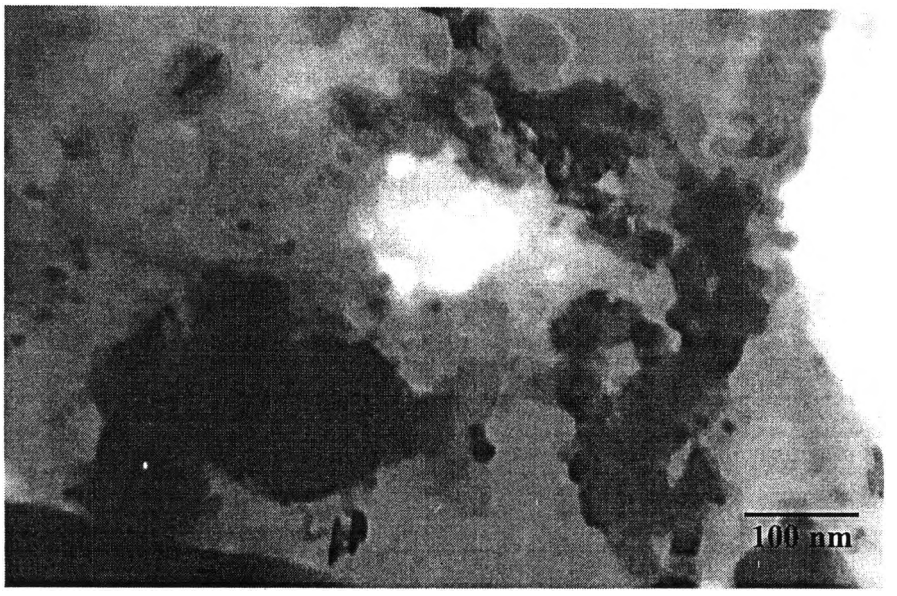

Figure 5.10(d) TEM photograph of the product at starting Zn/Ga = 0.50 synthesized in 2-propanol after calcination at 1100°C.

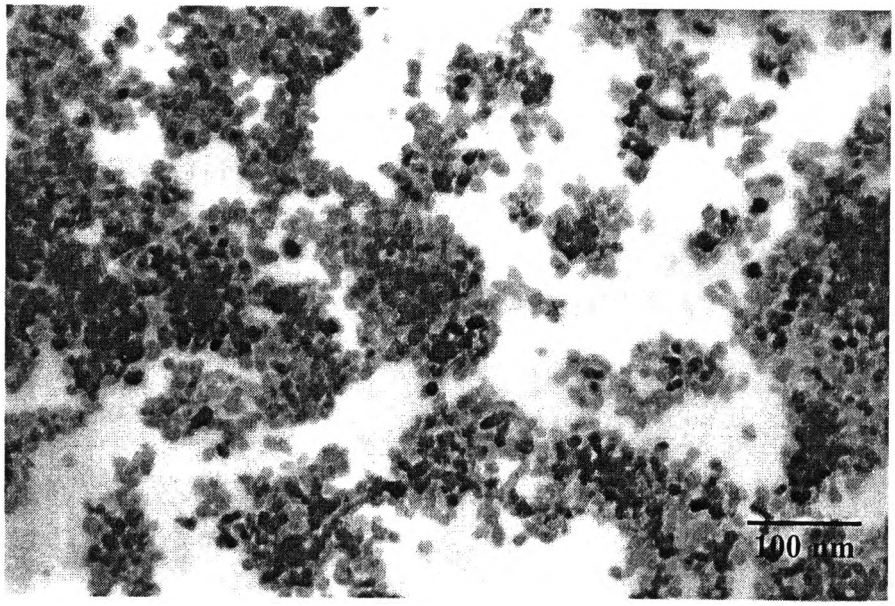

Figure 5.10(e) TEM photograph of the product at starting Zn/Ga = 0.33 synthesized in 2-propanol.

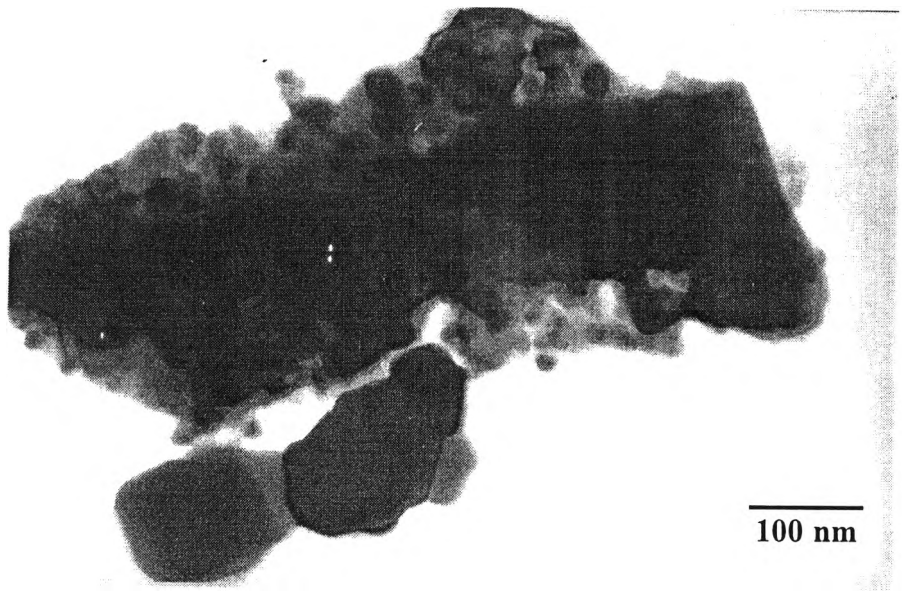

Figure 5.10(f) TEM photograph of the product at starting Zn/Ga = 0.33 synthesized in 2-propanol after calcination at 1100°C.

Table 5.2 BET surface area and crystallite size of the products synthesized by 2-propanol and the samples calcined at various temperatures.

Charged Zn/Ga ratio	S_{BET}[a](m^2/g)				d[b] (nm)				d[c] (nm)			
	as-syn	600°C	800°C	1100°C	as-syn	600°C	800°C	1100°C	as-syn	600°C	800°C	1100°C
0.33	82.15	62.15	25.17	8.94	8.13	11.33	65.12	433.13	8.33	11.33	65.33	433.15
0.50	79.63	19.91	15.93	12.61	8.12	10.63	64.16	473.34	8.00	10.67	64.33	473.33
1.00	85.97	71.93	22.01	7.24	8.65	17.38	69.51	491.16	8.67	17.33	69.67	491.15

[a]BET surface area.

[b]Crystallite size of the products calculated from Scherer equation using KCl as an internal standard

[c]Crystallite size of the products from TEM photograph.

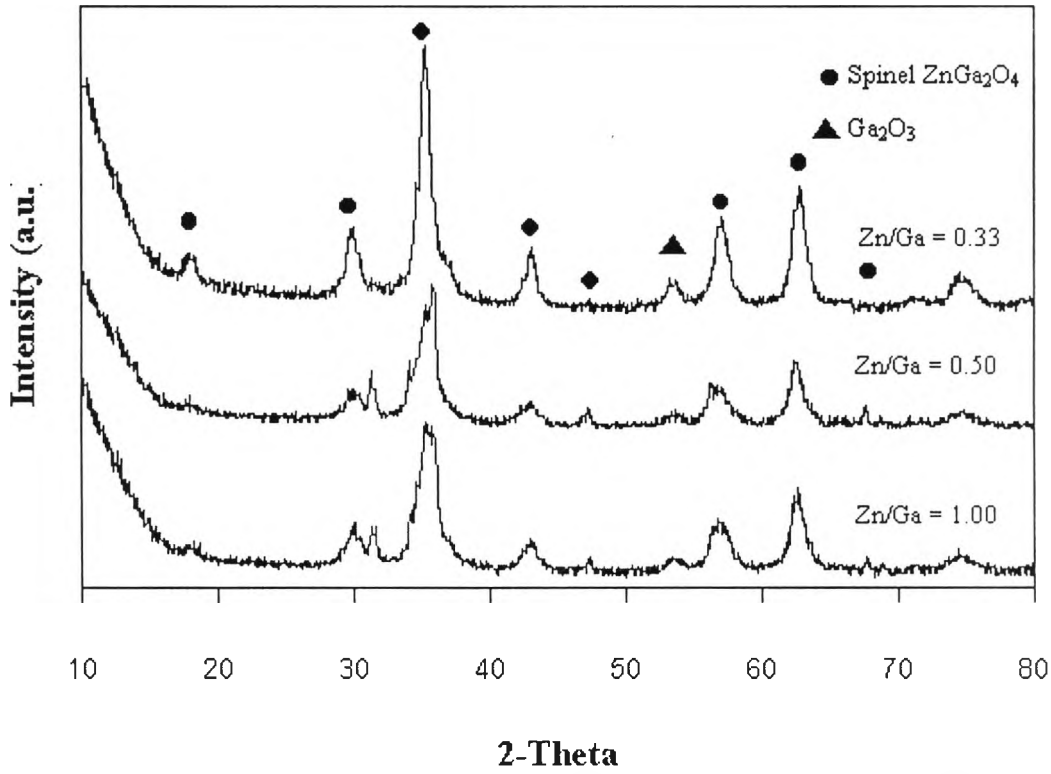

Figure 5.11 The XRD patterns of the zinc gallate products at various starting Zn/Ga ratios synthesized in 1-butanol.

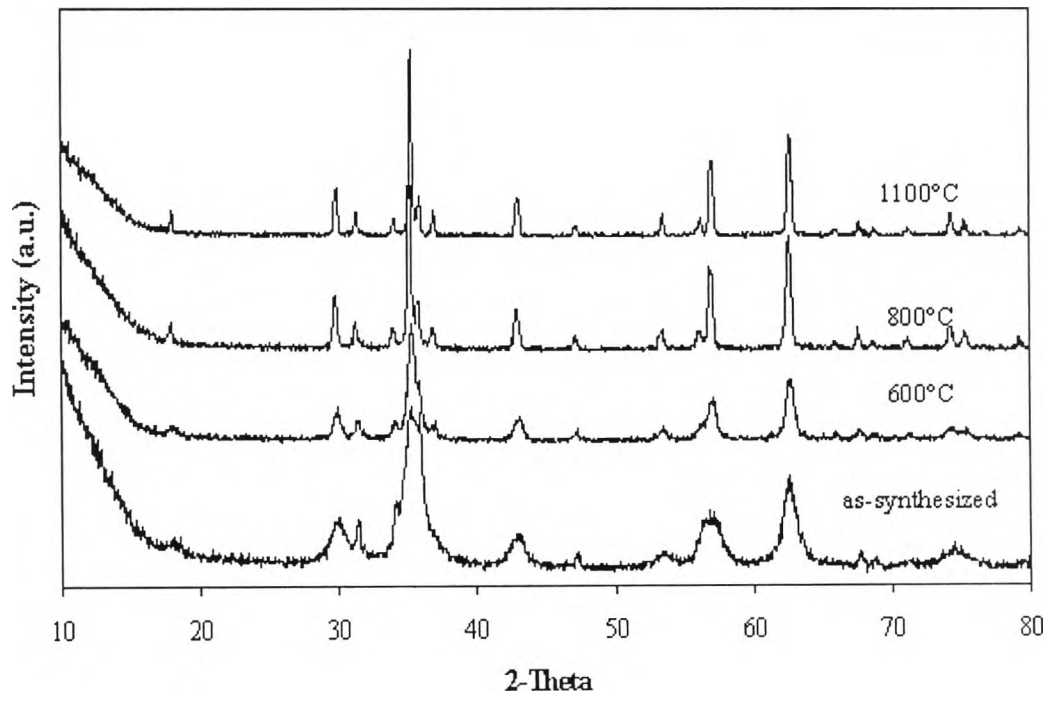

Figure 5.12 The XRD patterns of the products at starting Zn/Ga = 1.00 synthesized in 1-butanol before and after calcination at 600, 800, 1100°C.

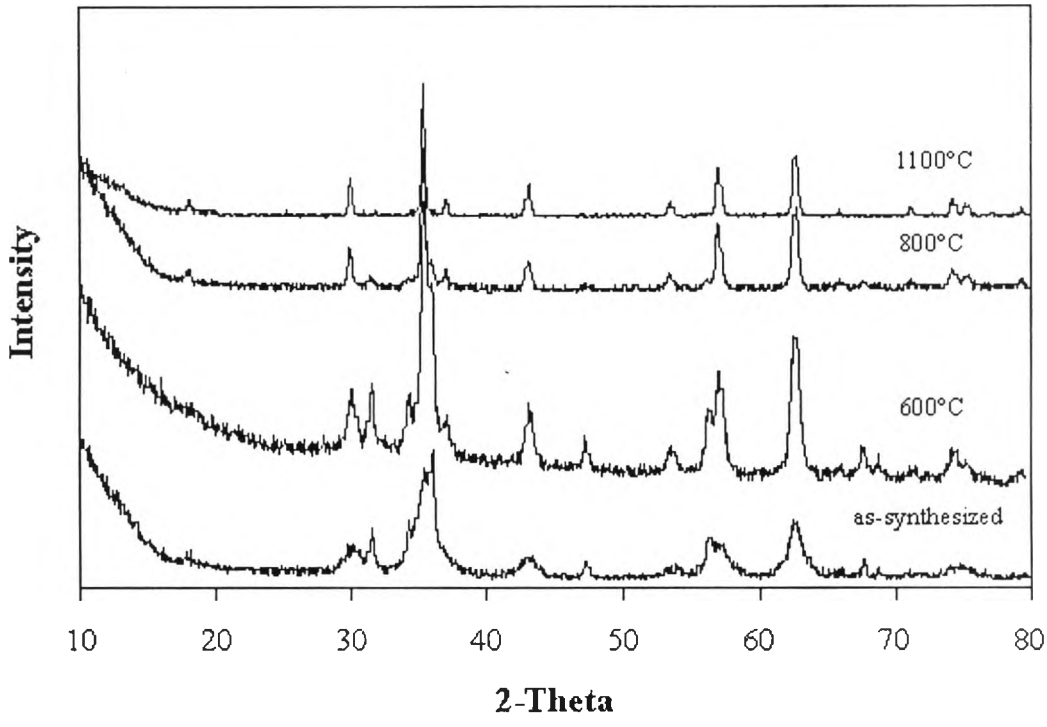

Figure 5.13 The XRD patterns of the products at starting Zn/Ga = 0.50 synthesized in 1-butanol before and after calcination at 600,800, and 1100°C.

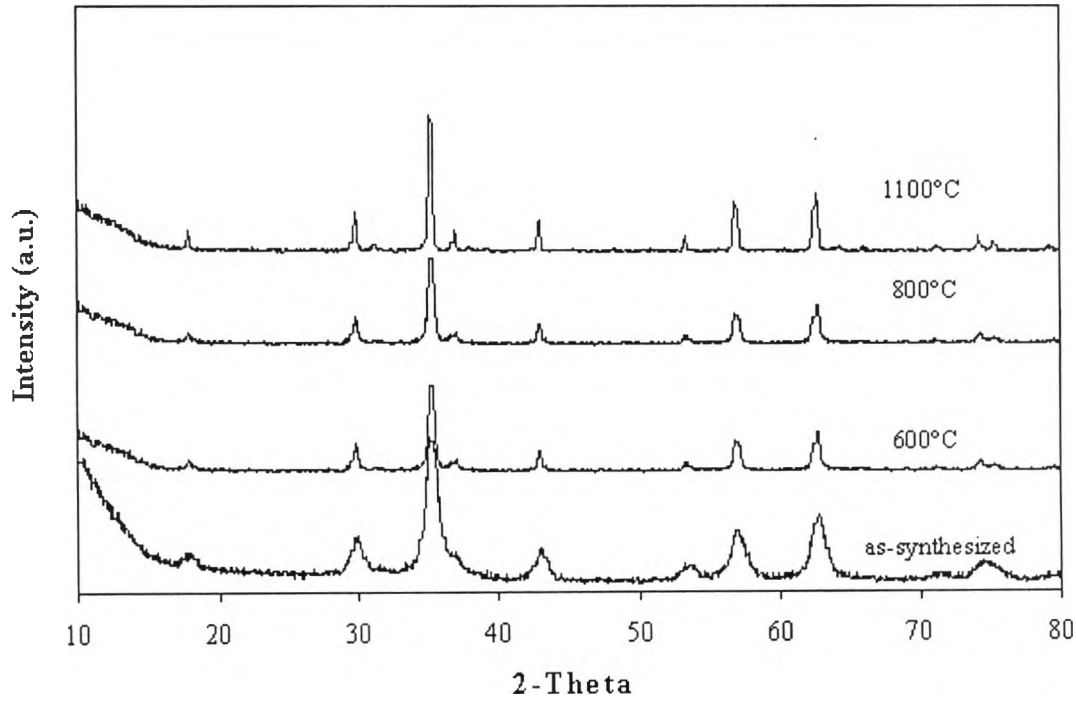

Figure 5.14 The XRD patterns of the products at starting Zn/Ga = 0.33 synthesized in 1-butanol before and after calcination at 600, 800, and 1100°C.

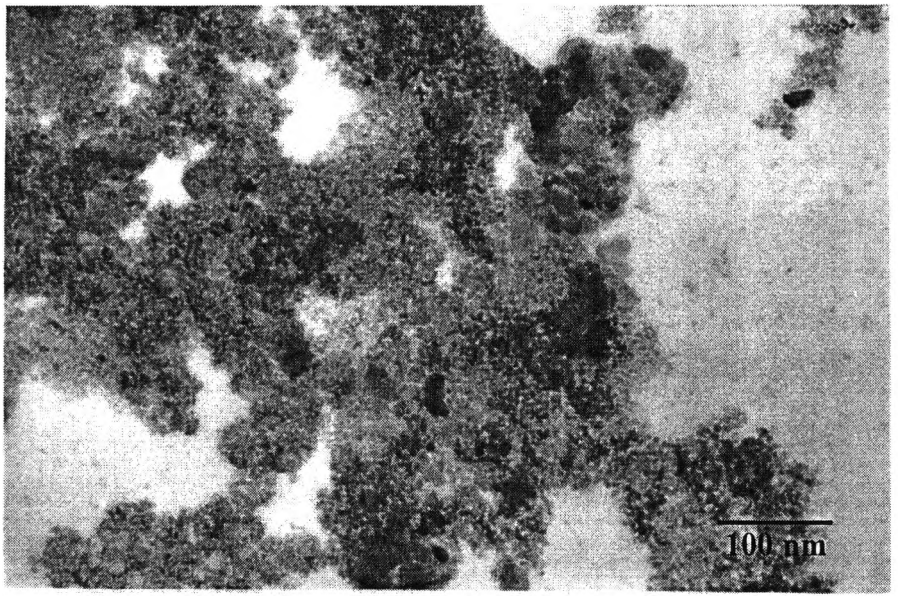

Figure 5.15(a) TEM photograph of the product at starting Zn/Ga = 1.00 synthesized in 1-butanol.

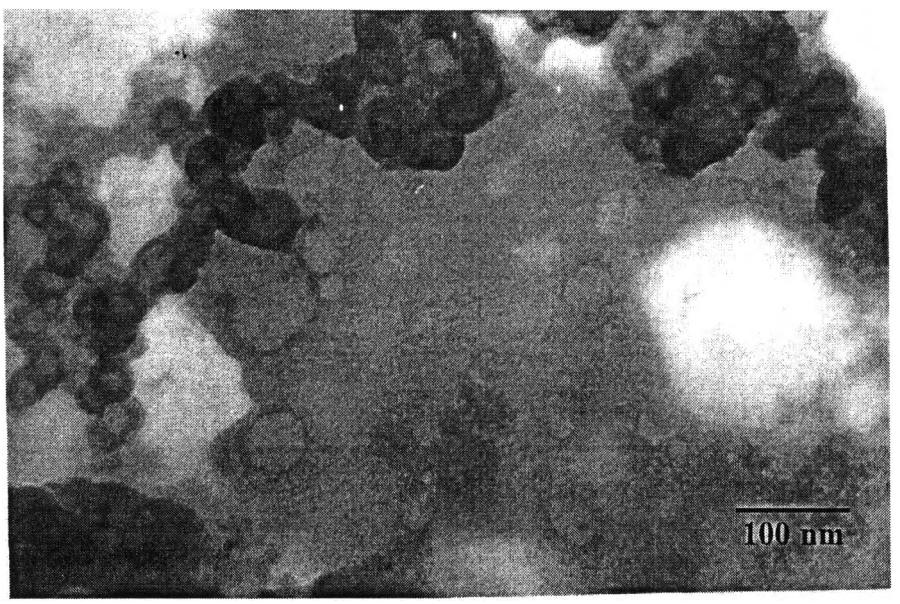

Figure 5.15(b) TEM photograph of the product at starting Zn/Ga = 1.00 synthesized in 1-butanol after calcination at 1100°C.

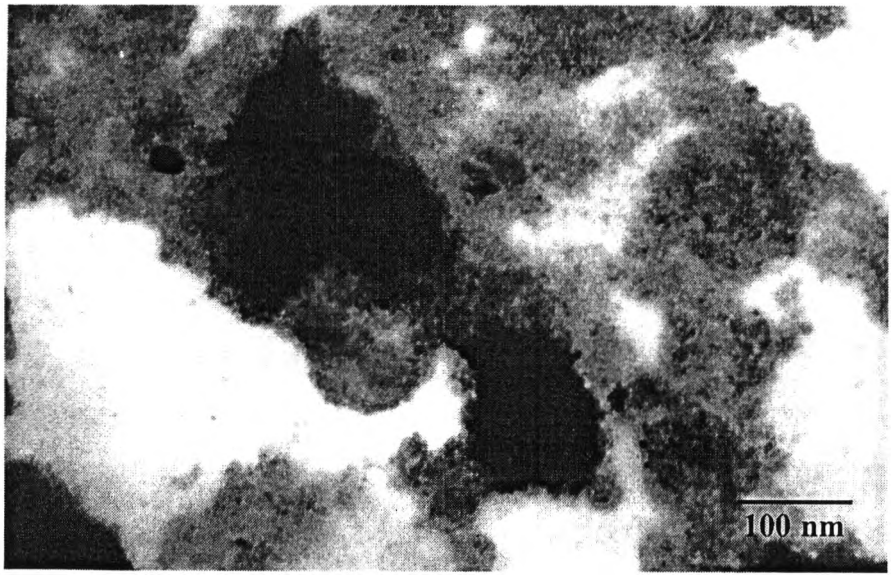

Figure 5.15(c) TEM photograph of the product at Zn/Ga = 0.50 synthesized in 1-butanol .

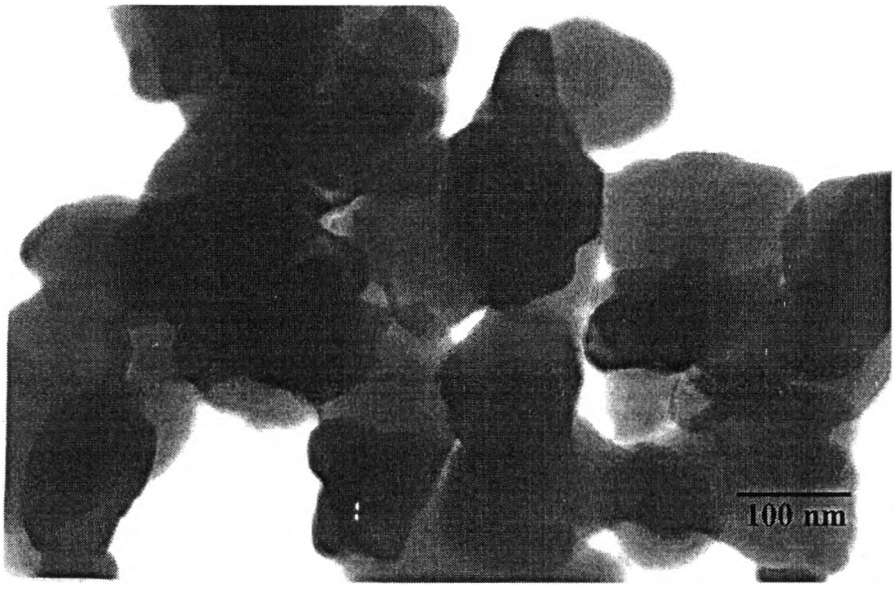

Figure 5.15(d) TEM photograph of the product at starting Zn/Ga = 0.50 synthesized in 1-butanol after calcination at 1100°C.

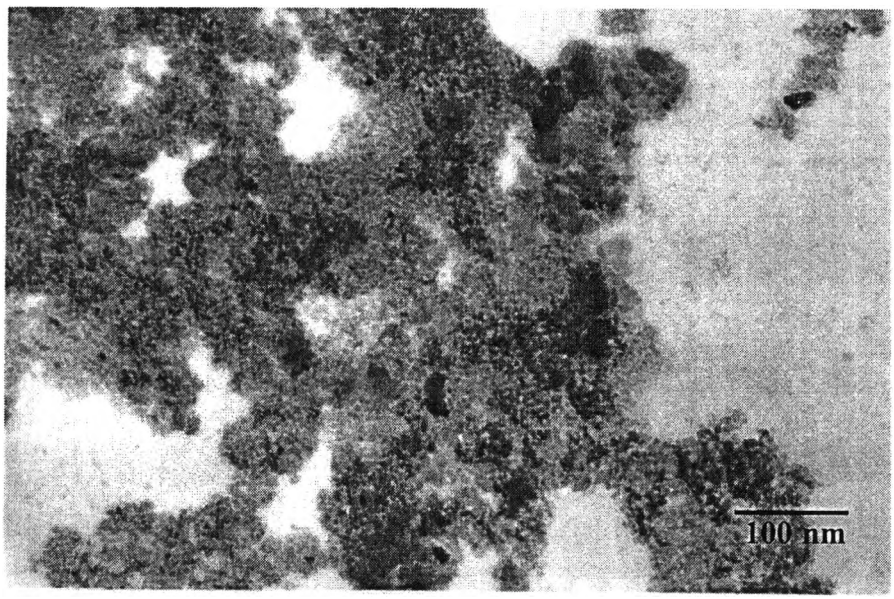

Figure 5.15(e) TEM photograph of the product at starting Zn/Ga = 0.33 synthesized in 1-butanol.

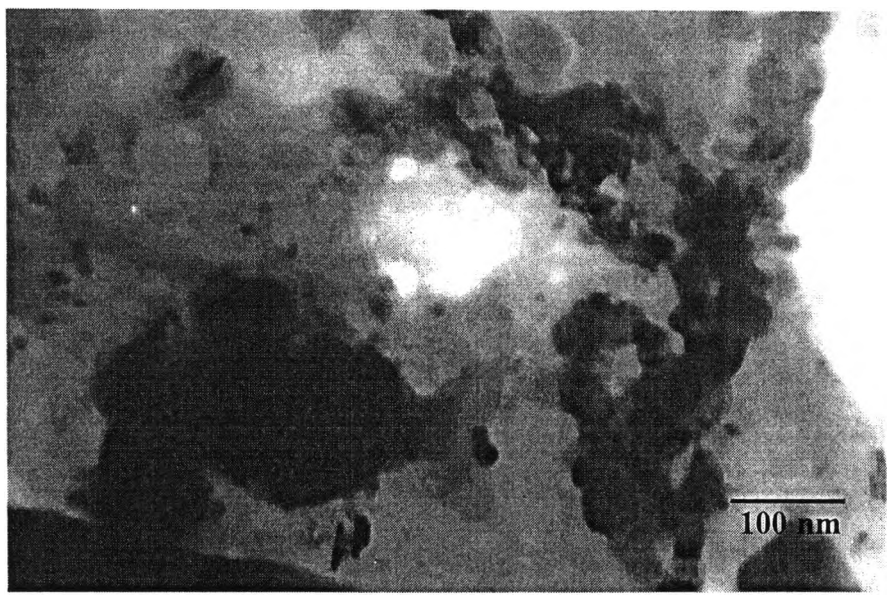

Figure 5.15(f) TEM photograph of the product at starting Zn/Ga = 0.33 synthesized in 1-butanol after calcination at 1100°C.

Table 5.3 BET surface area and crystallite size of the products synthesized by 1-butanol and the samples calcined at various temperatures.

Charged Zn/Ga ratio	S_{BET}[a](m^2/g)				d[b] (nm)				d[c] (nm)			
	as-syn	600°C	800°C	1100°C	as-syn	600°C	800°C	1100°C	as-syn	600°C	800°C	1100°C
0.33	117.70	82.42	45.59	16.24	6.67	13.19	46.34	113.34	6.37	13.33	46.33	113.15
0.50	113.42	21.55	13.61	7.94	8.98	14.20	50.57	151.76	8.99	14.33	50.33	151.67
1.00	116.87	79.16	15.14	13.56	6.87	14.67	50.57	117.48	6.67	14.67	50.67	117.15

[a]BET surface area.

[b]Crystallite size of the products calculated from Scherer equation using KCl as an internal standard

[c]Crystallite size of the products from TEM photograph.

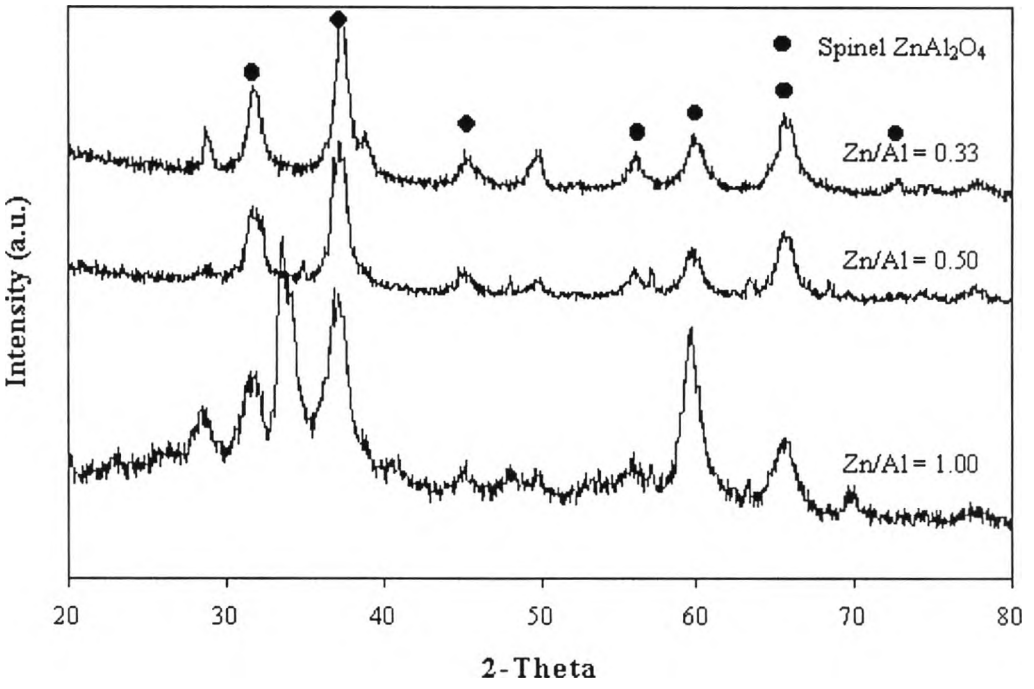

Figure 5.16 The XRD patterns of the zinc aluminate products at various starting Zn/Al ratios synthesized in 1,4-butanediol.

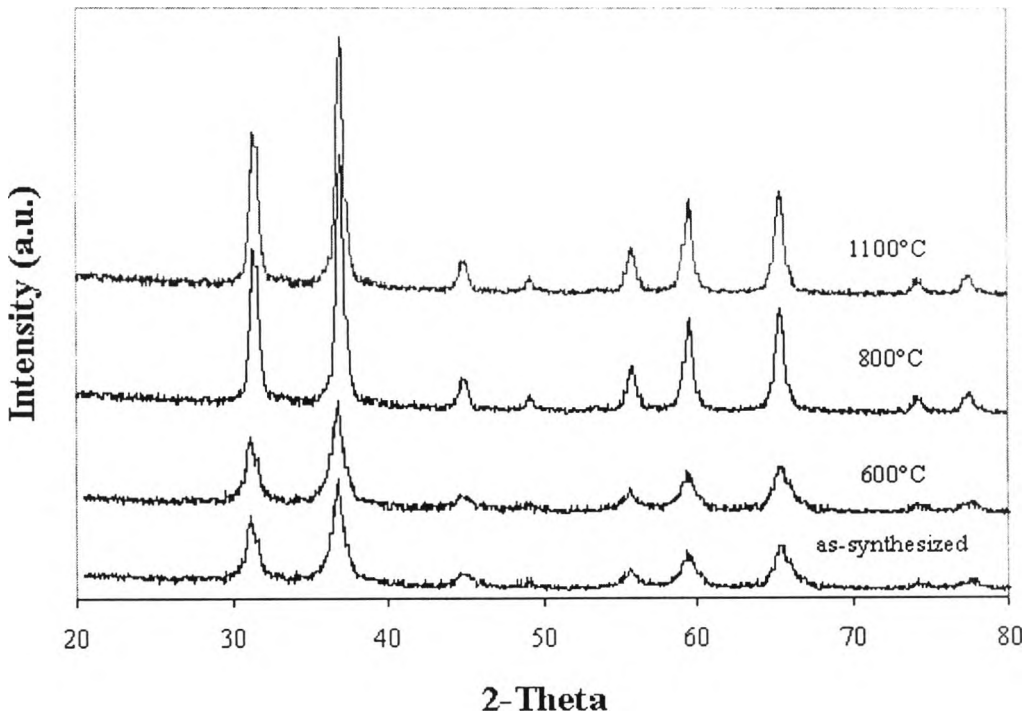

Figure 5.17 The XRD patterns of the products at starting Zn/Al = 1.00 synthesized in 1,4-butanediol before and after calcination at 600°C, 800°C, and 1100°C.

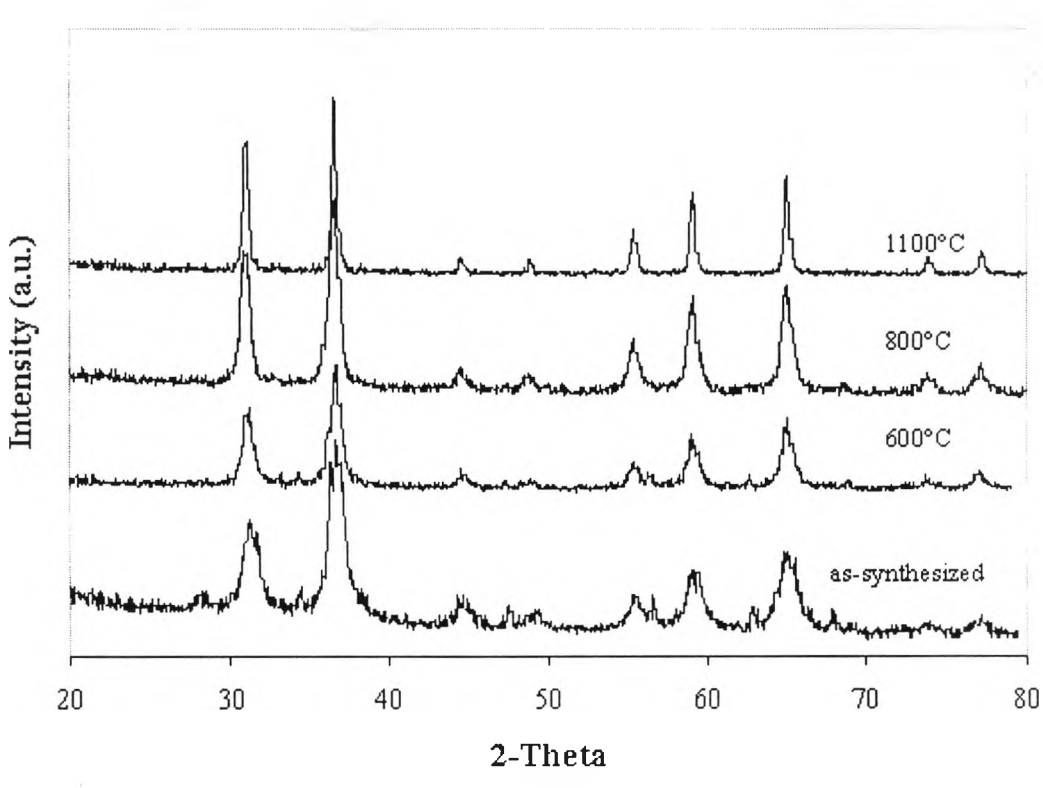

Figure 5.18 The XRD patterns of the products at starting Zn/Al = 0.50 synthesized in 1,4-butanediol before and after calcination at 600, 800, and 1100°C.

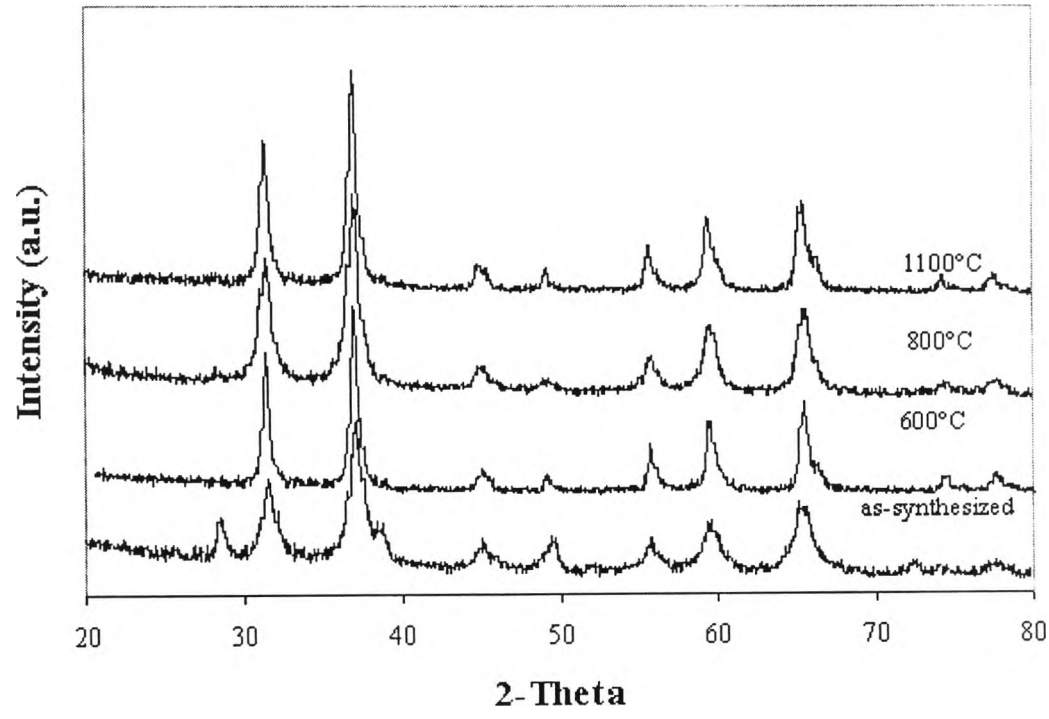

Figure 5.19 The XRD patterns of the products at the starting Zn/Al = 0.33 synthesized in 1,4-butanediol before and after calcination at 600, 800, and 1100°C.

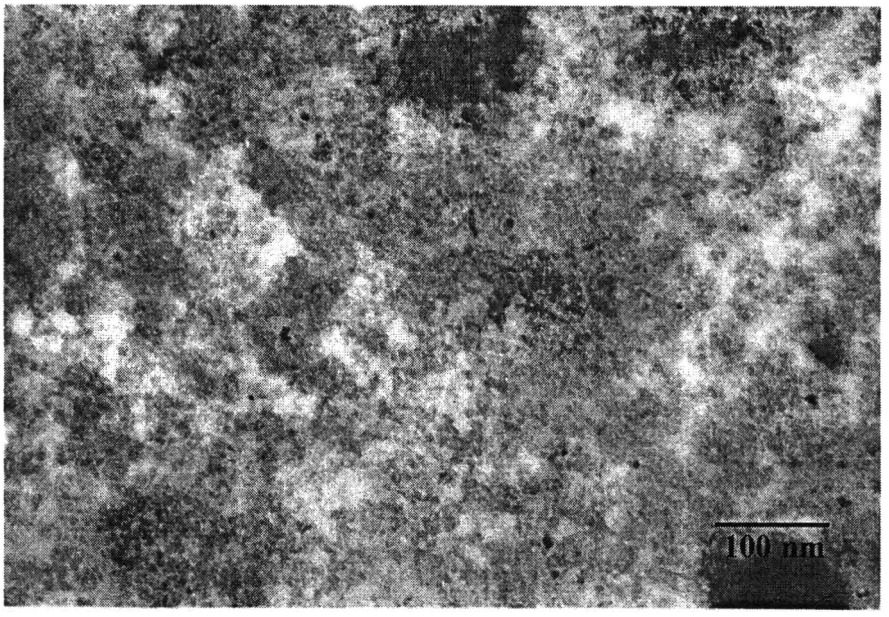

Figure5.20(a) TEM photograph of the product at Zn/Al=1.00 synthesized in 1,4-butanediol

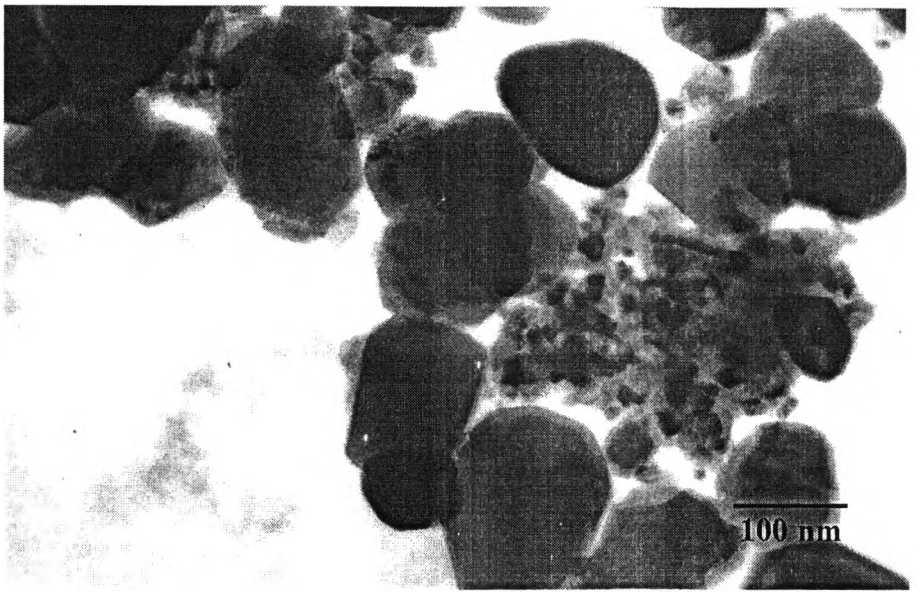

Figure5.20(b) TEM photograph of the product at Zn/Al=1.00 synthesized in 1,4-butanediol after calcination at 1100°C.

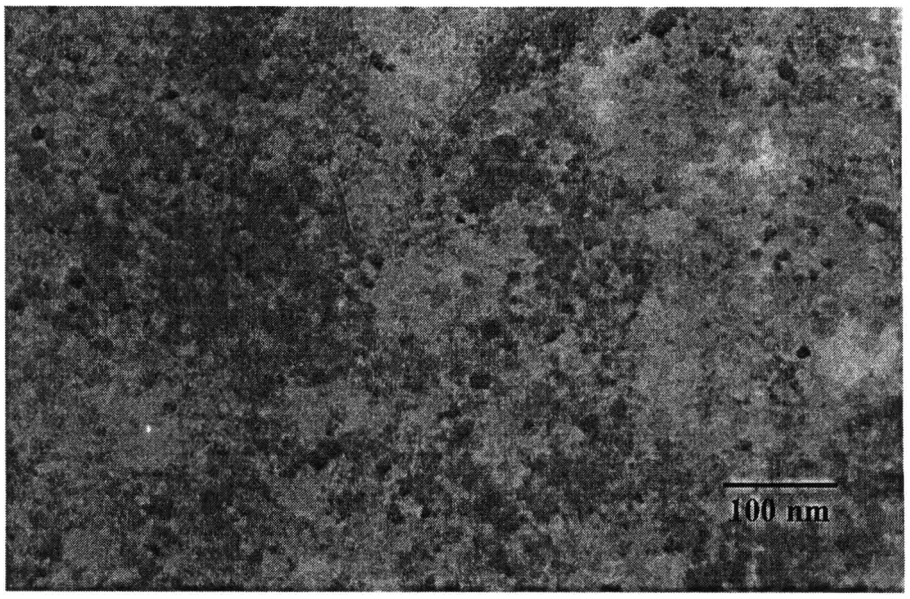

Figure 5.20 (c) TEM photograph of the product at Zn/Al = 0.50 synthesized in 1,4-butanediol.

Figure 5.20(d) TEM photograph of the product synthesized at Zn/Al = 0.50 in 1,4-butanediol after calcination at 1100°C.

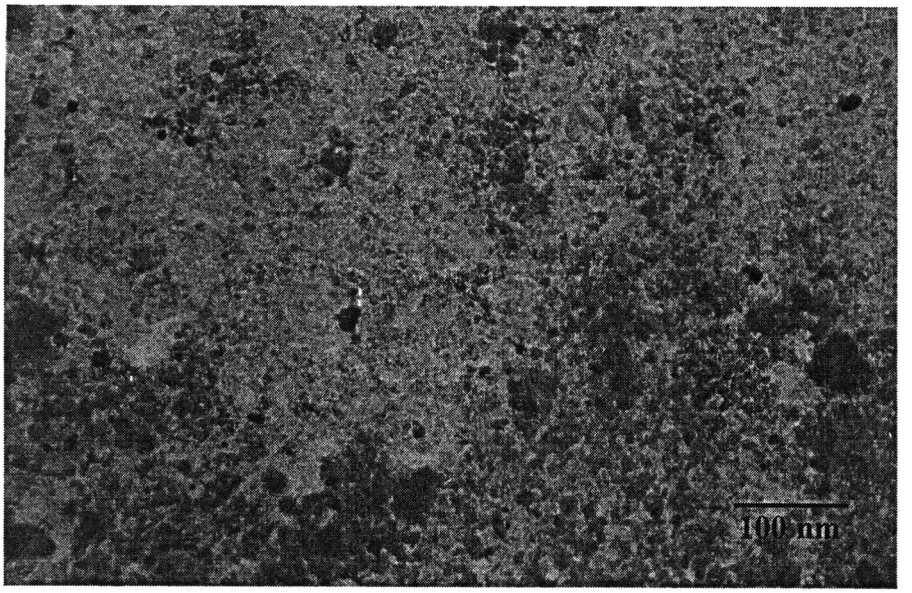

Figure 5.20(e) TEM photograph of the product at Zn/Al = 0.33 synthesized in 1,4-butanediol.

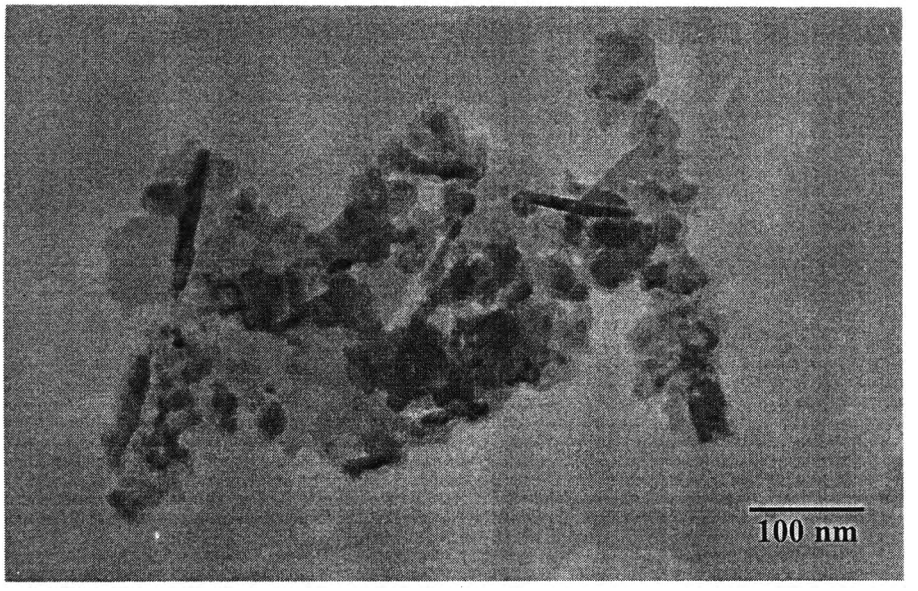

Figure 5.20(f) TEM photograph of the product at Zn/Al=0.33 synthesized in 1,4-butanediol after calcination at 1100°C

Table 5.4 BET surface area and crystallite size of the products synthesized by 1,4-butanediol and the samples calcined at various temperatures.

Charged Zn/Al ratio	S_{BET}[a] (m^2/g)				d[b] (nm)				d[c] (nm)			
	as-syn	600°C	800°C	1100°C	as-syn	600°C	800°C	1100°C	as-syn	600°C	800°C	1100°C
0.33	156.35	129.93	74.86	41.82	7.98	17.21	24.21	79.41	7.99	17.33	24.33	79.15
0.50	155.68	85.62	50.05	21.39	9.81	18.20	54.78	79.72	9.67	18.67	54.33	79.33
1.00	86.72	60.43	31.15	5.45	12.36	21.24	98.35	110.31.	12.67	21.33	98.67	110.15

[a]BET surface area.

[b]Crystallite size of the products calculated from Scherer equation using KCl as an internal standard

[c]Crystallite size of the products from TEM photograph.

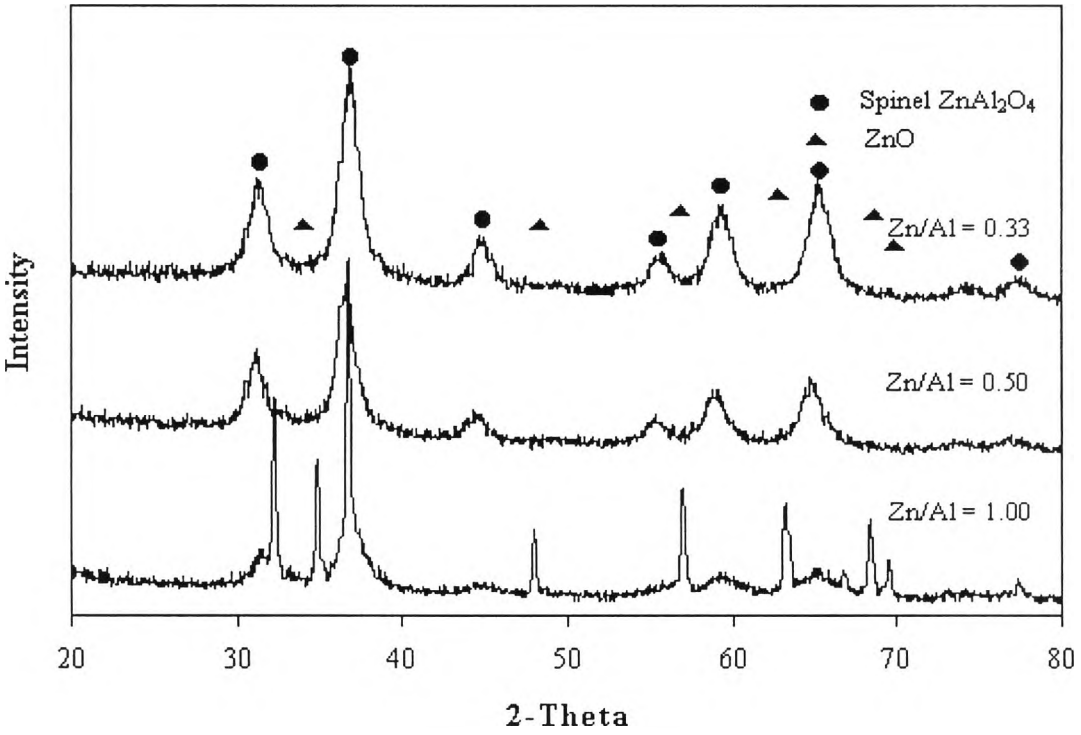

Figure 5.21 The XRD patterns of the zinc aluminate products at various starting Zn/Al synthesized in toluene.

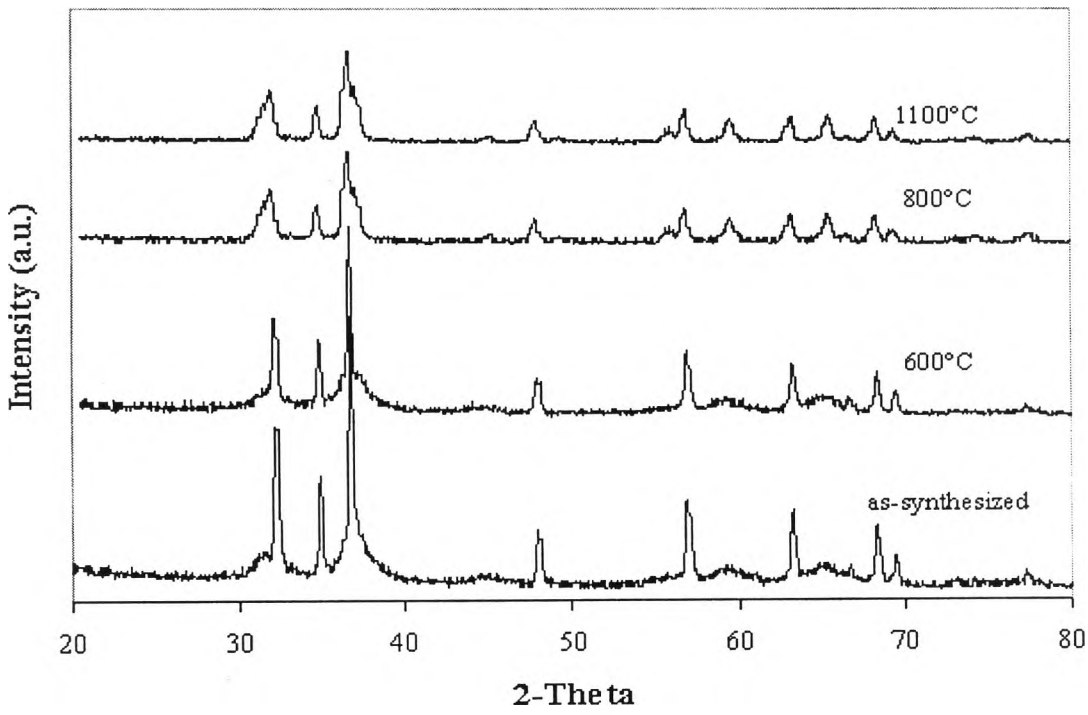

Figure 5.22 The XRD patterns of the products at the starting Zn/Al = 1.00 synthesized in toluene before and after calcination at 600, 800, and 1100°C.

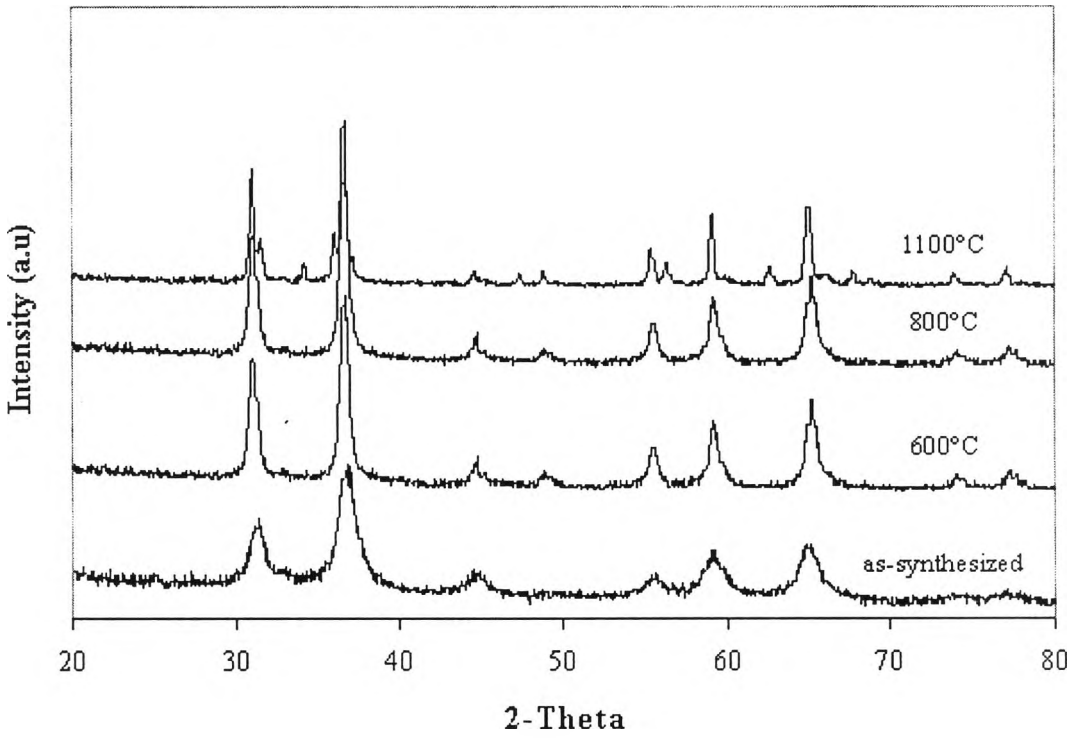

Figure 5.23 The XRD patterns of the products at the starting Zn/Al = 0.50 synthesized in toluene before and after calcination at 600, 800, and 1100°C.

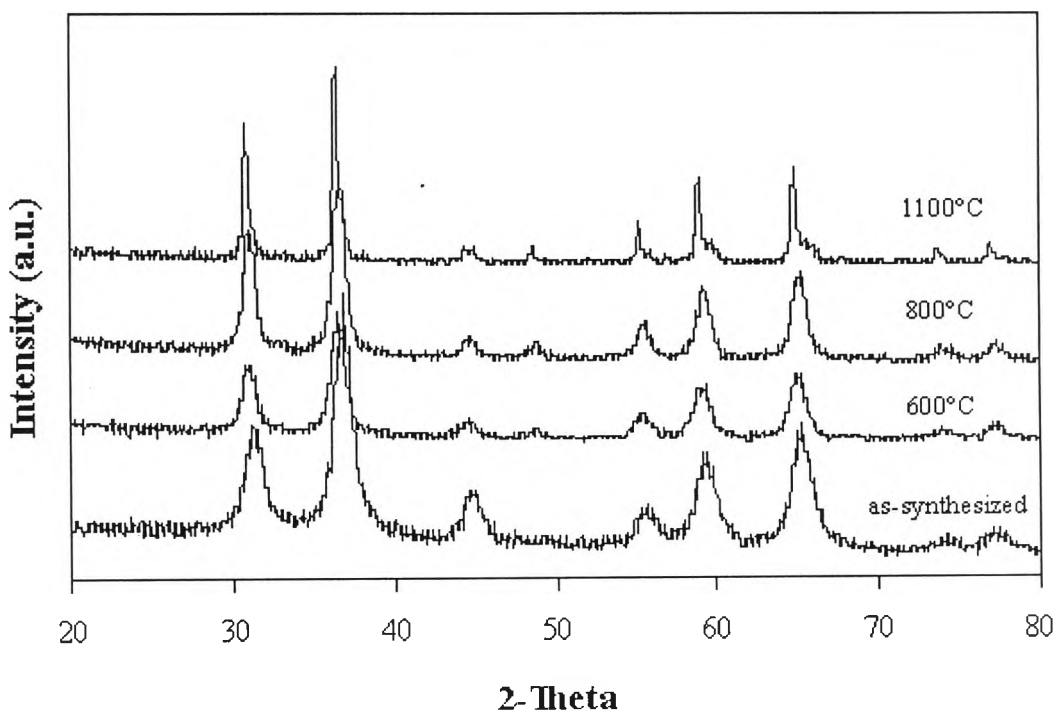

Figure 5.24 The XRD patterns of the products at the starting Zn/Al = 0.33 synthesized in toluene before and after calcination at 600, 800, and 1100°C.

Figure5.25(a) TEM photograph of the product at Zn/Al=1.00 synthesized in toluene

Figure 5.20(b) TEM photograph of the product at Zn/Al=1.00 synthesized in toluene after calcination at 1100°C.

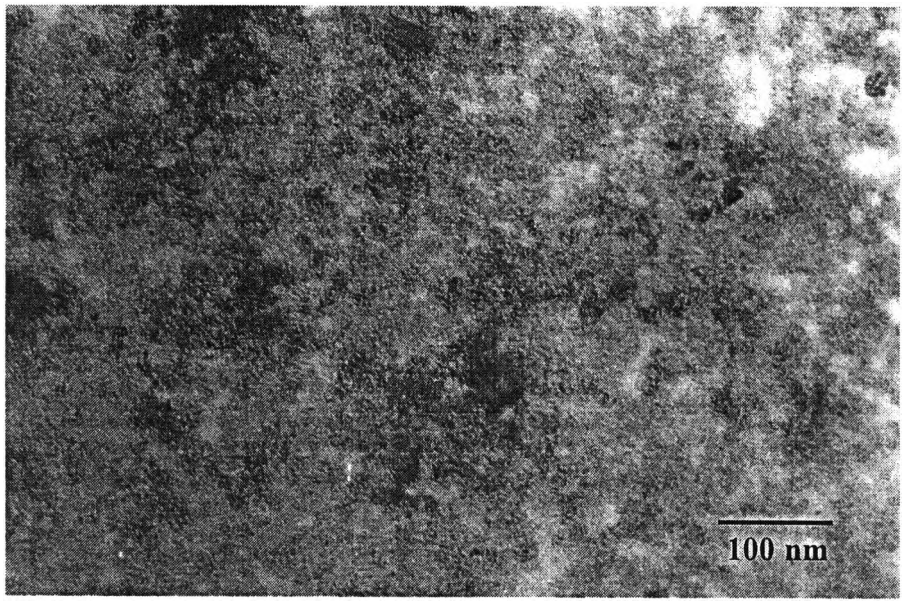

Figure 5.25(c) TEM photograph of the product at Zn/Al= 0.50 synthesized in toluene

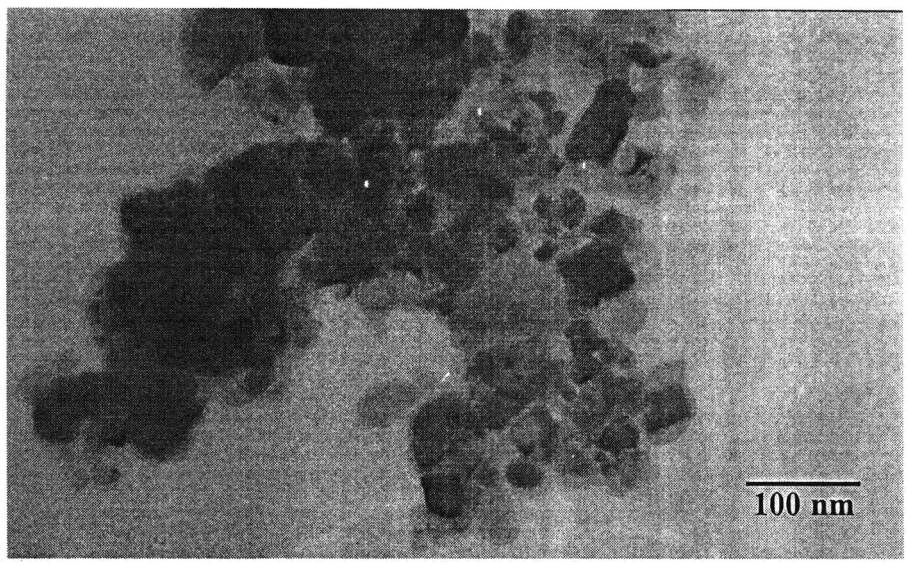

Figure5.25(d) TEM photograph of the product at Zn/Al = 0.50 synthesized in toluene after calcination at 1100°C

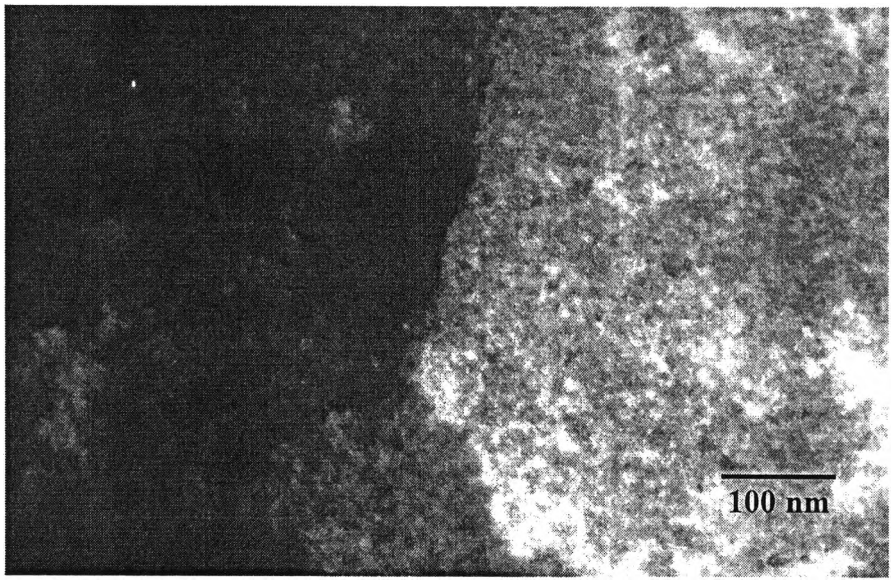

Figure 5.25 (e) TEM photograph of the product at Zn/Al = 0.33 synthesized in toluene.

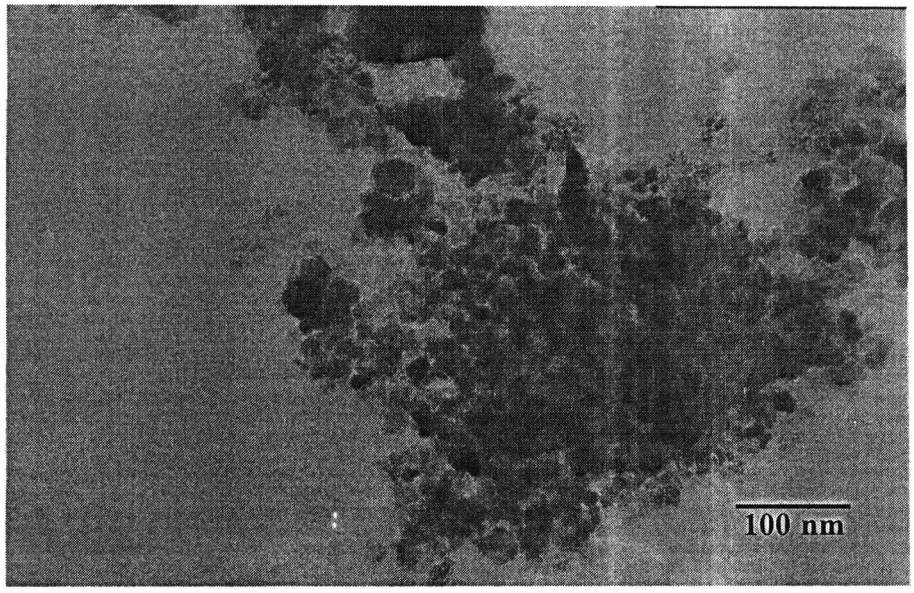

Figure 5.25(f) TEM photograph of the product at Zn/Al = 0.33 synthesized in toluene after calcination at 1100°C.

Table 5.5 BET surface area and crystallite size of the products synthesized by toluene and the samples calcined at various temperatures.

Charged Zn/Al ratio	S_{BET}[a](m^2/g)				d[b] (nm)				d[c] (nm)			
	as-syn	600°C	800°C	1100°C	as-syn	600°C	800°C	1100°C	as-syn	600°C	800°C	1100°C
0.33	220.88	158.43	65.26	13.06	6.33	10.81	23.42	136.96	6.33	11.15	23.33	137.15
0.50	197.11	88.70	33.51	15.77	7.35	10.66	27.46	110.33	7.33	10.67	27.33	111.33
1.00	213.03	54.12	19.80	13.59	6.67	12.13	23.89	139.64	6.67	12.33	23.99	139.99

[a]BET surface area.

[b]Crystallite size of the products calculated from Scherer equation using KCl as an internal standard

[c]Crystallite size of the products from TEM photograph.

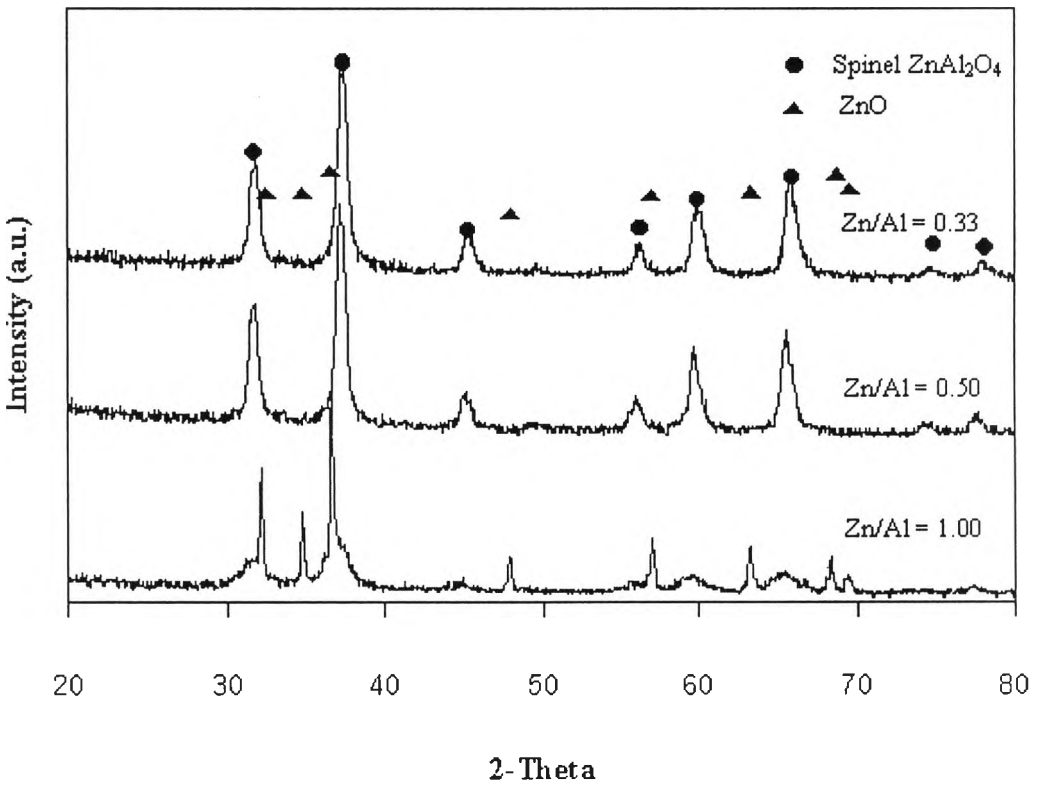

Figure 5.26 The XRD patterns of the zinc aluminate products at various the starting Zn/Al synthesized in 2-propanol.

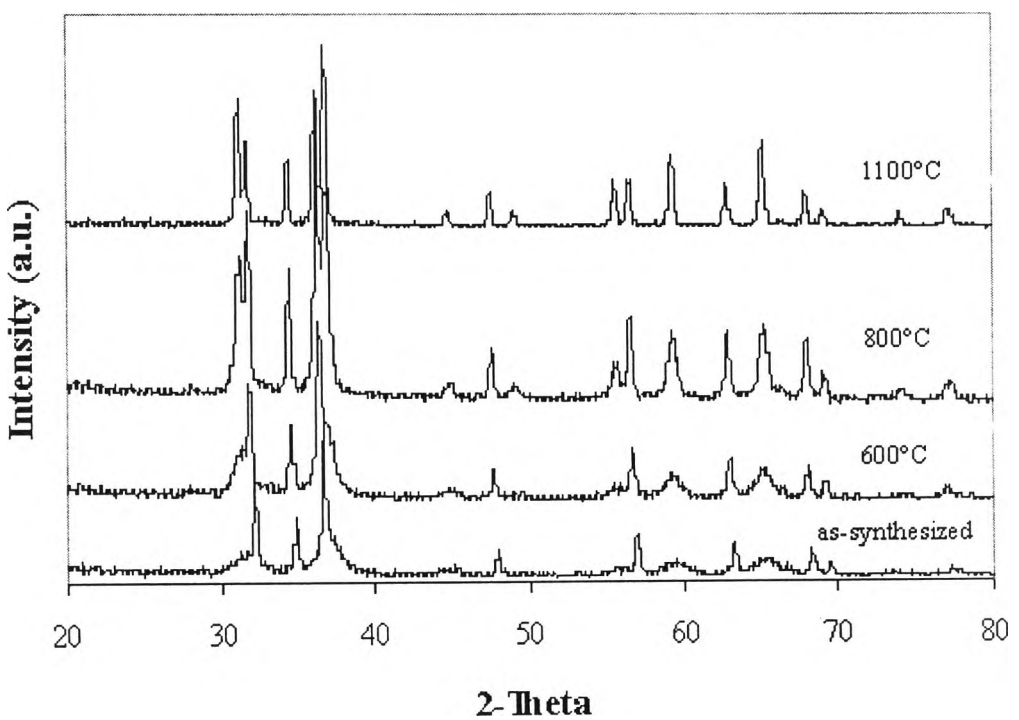

Figure 5.27 The XRD patterns of the products at the starting Zn/Al = 1.00 synthesized in 2-propanol before and after calcination at 600, 800, and 1100°C.

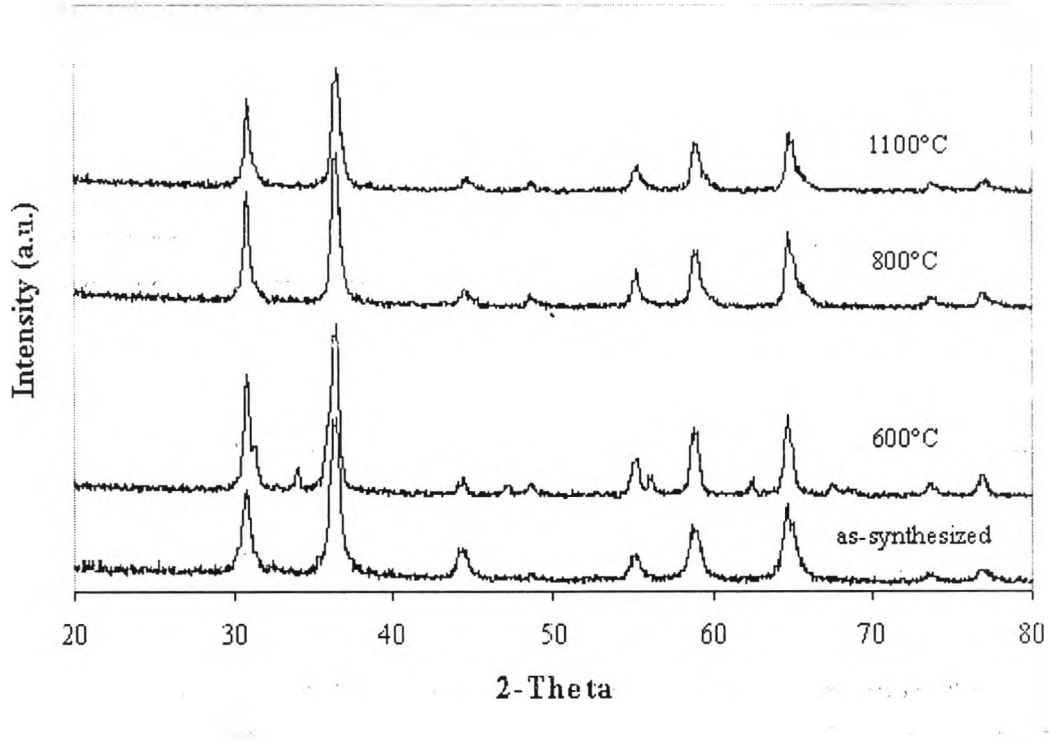

Figure 5.28 The XRD patterns of the products at the starting Zn/Al = 0.50 synthesized in 2-propanol before and after calcination at 600, 800, and 1100°C.

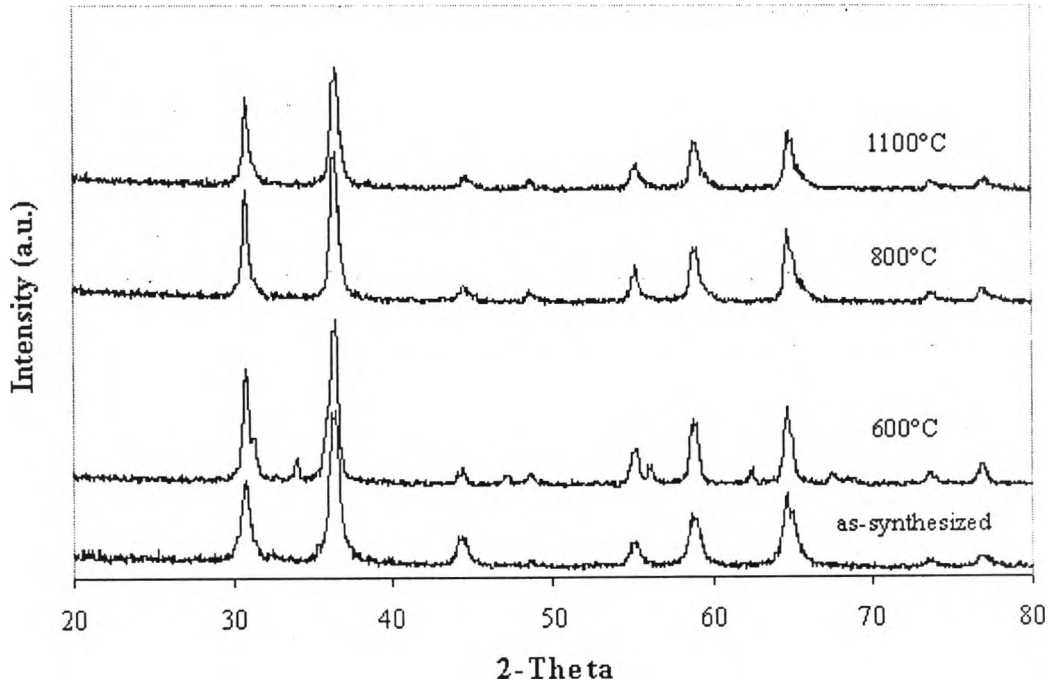

Figure 5.29 The XRD patterns of the products at the starting Zn/Al = 0.33 synthesized in 2-propanol before and after calcination at 600, 800, and 1100°C.

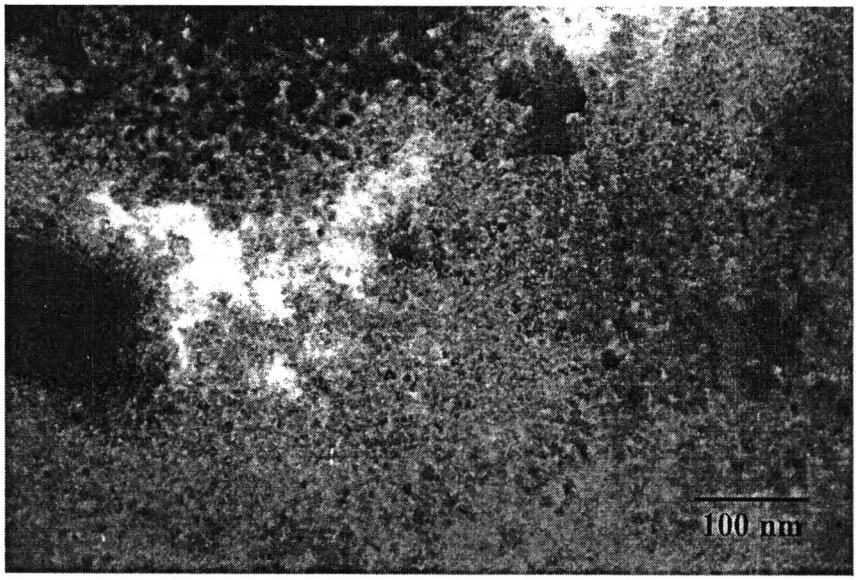

Figure 5.30(a) TEM photograph of the product at starting Zn/Al = 1.00 synthesized in 2-propanol .

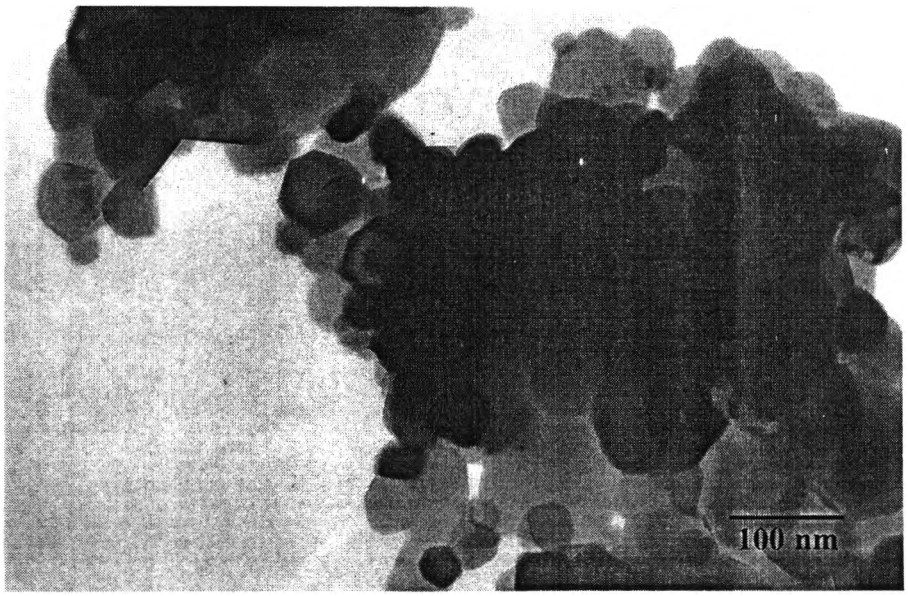

Figure 5.30(b) TEM photograph of the product at starting Zn/Al = 1.00 synthesized in 2-propanol after calzination at 1100°C.

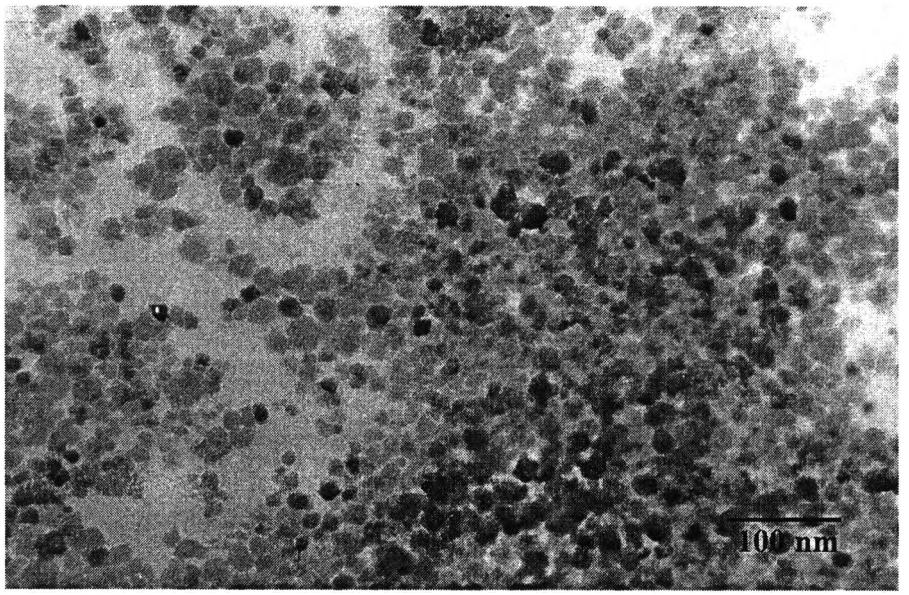

Figure 5.30(c) TEM photograph of the product at Zn/Al = 0.50 synthesized in 2-propanol.

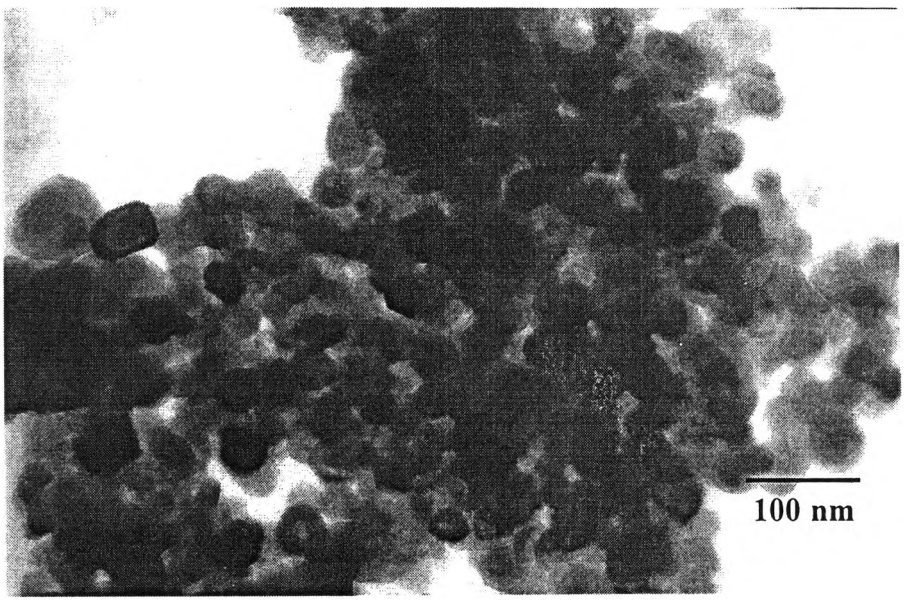

Figure 5.30 (d) TEM photograph of the product at Zn/Al = 0.50 synthesized in 2-propanol after calcination at 1100°C.

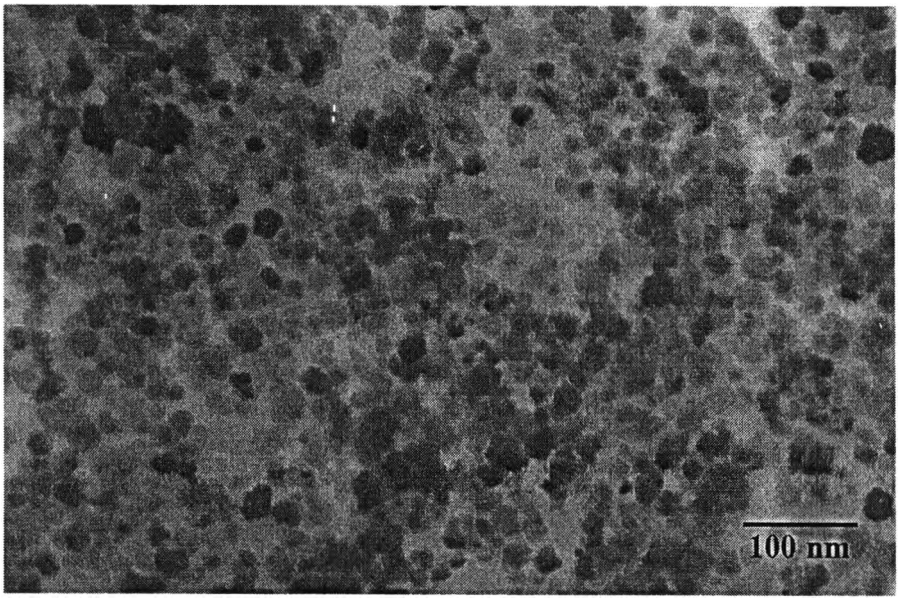

Figure 5.30(e) TEM photograph of the product at Zn/Al = 0.33 synthesized in 2-propanol.

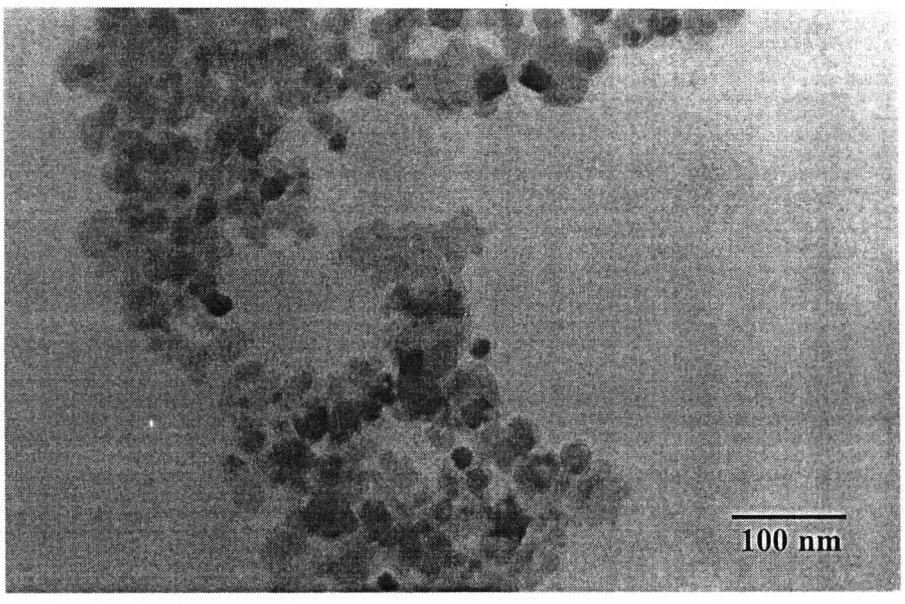

Figure 5.30(f) TEM photograph of the product at Zn/Al = 0.33 synthesized in 2-propanol calcination at 1100°C.

Table 5.6 BET surface area and crystallite size of the products synthesized by 2-propanol and the samples calcined at various temperatures.

Charged Zn/Al ratio	S_{BET}[a](m^2/g)				d[b] (nm)				d[c] (nm)			
	as-syn	600°C	800°C	1100°C	as-syn	600°C	800°C	1100°C	as-syn	600°C	800°C	1100°C
0.33	95.05	73.57	51.15	14.87	9.75	28.71	35.69	153.72	10.15	28.33	35.33	153.15
0.50	80.94	72.04	53.42	15.38	10.43	30.15	35.62	146.59	10.33	30.67	35.33	147.33
1.00	143.06	77.44	26.95	4.99	9.75	39.85	98.44	239.49	9.67	40.15	98.67	239.15

[a]BET surface area.

[b]Crystallite size of the products calculated from Scherer equation using KCl as an internal standard

[c]Crystallite size of the products from TEM photograph.

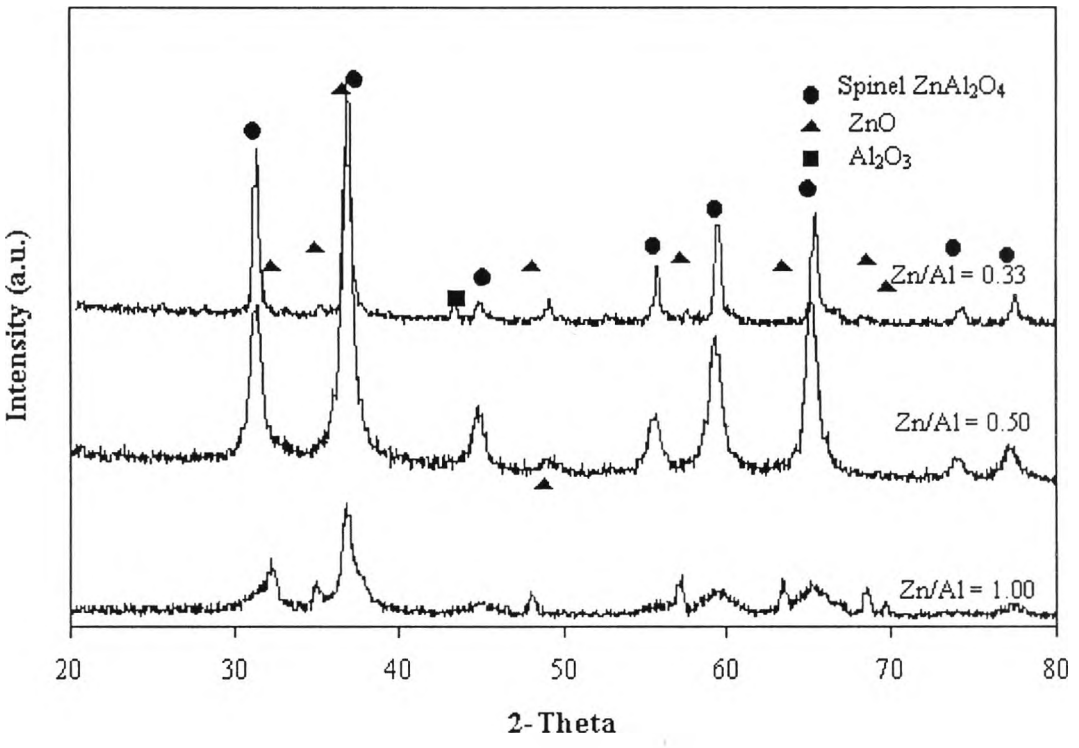

Figure 5.31 The XRD patterns of the zinc aluminate products at the various starting Zn/Al synthesized in 1-butanol.

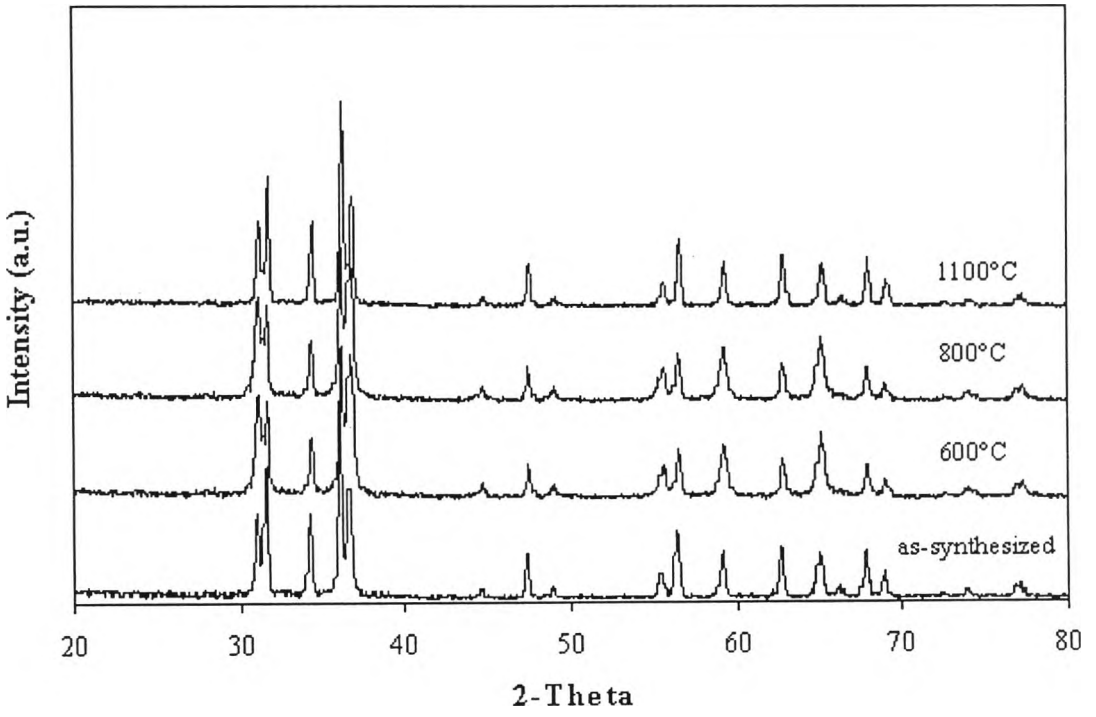

Figure 5.32 The XRD patterns of the products at the starting Zn/Al = 1.00 synthesized in 1-butanol before and after calcination at 600, 800, and 1100°C.

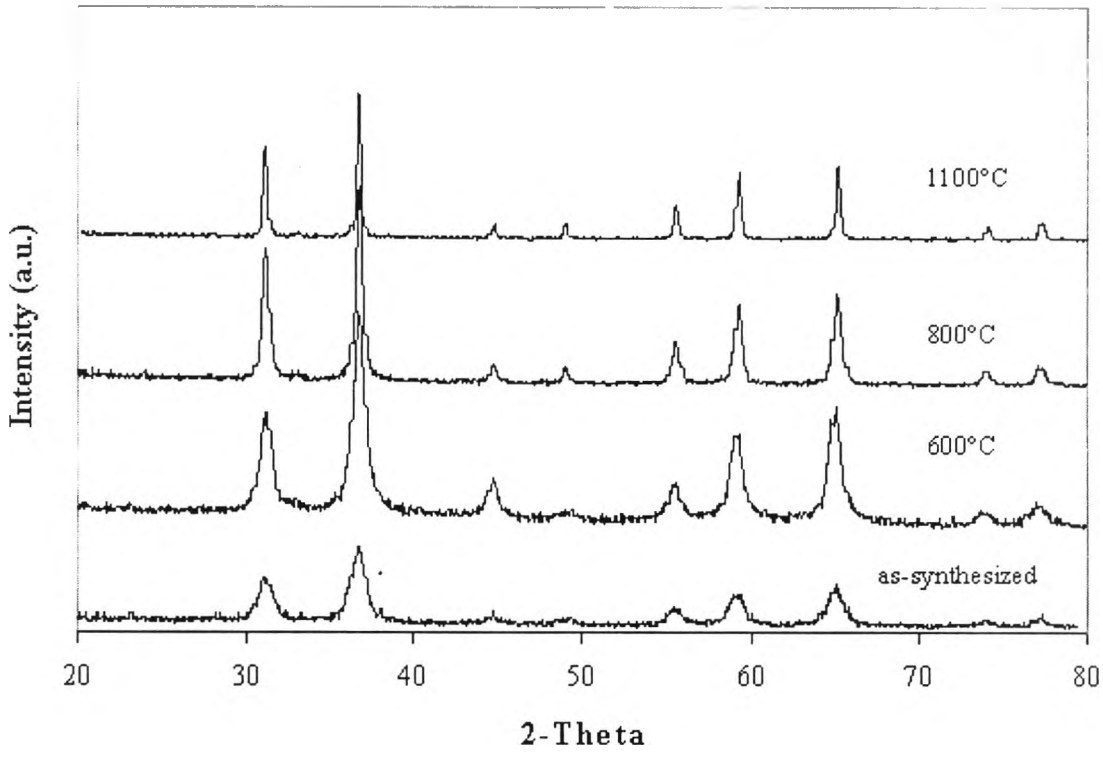

Figure 5.33 The XRD patterns of the products at starting Zn/Al = 0.50 synthesized in 1-butanol and after calcination at 600, 800 and 1100°C.

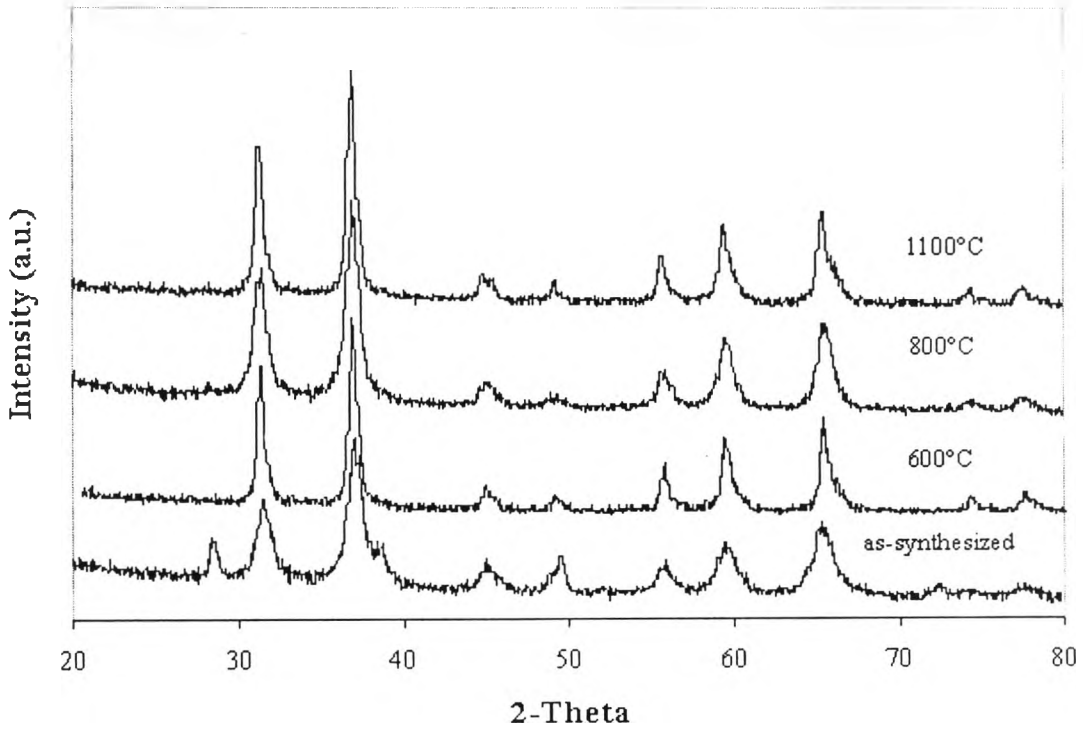

Figure 5.34 The XRD patterns of the products at the starting Zn/Al = 0.33 synthesized in 1-butanol before and after calcination at 600, 800, and 1100°C.

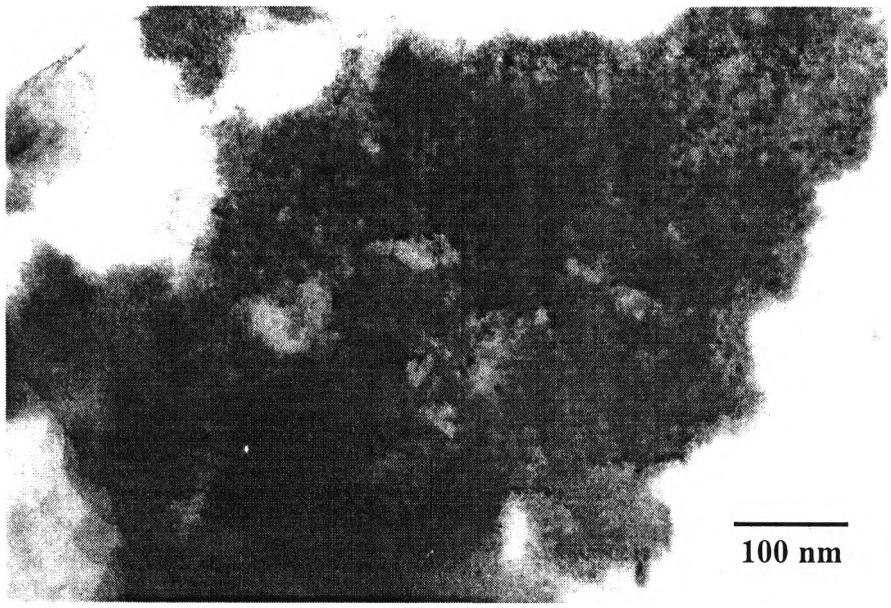

Figure 5.35 (a) TEM photograph of the product at Zn/Al=1.00 synthesized in 1-butanol.

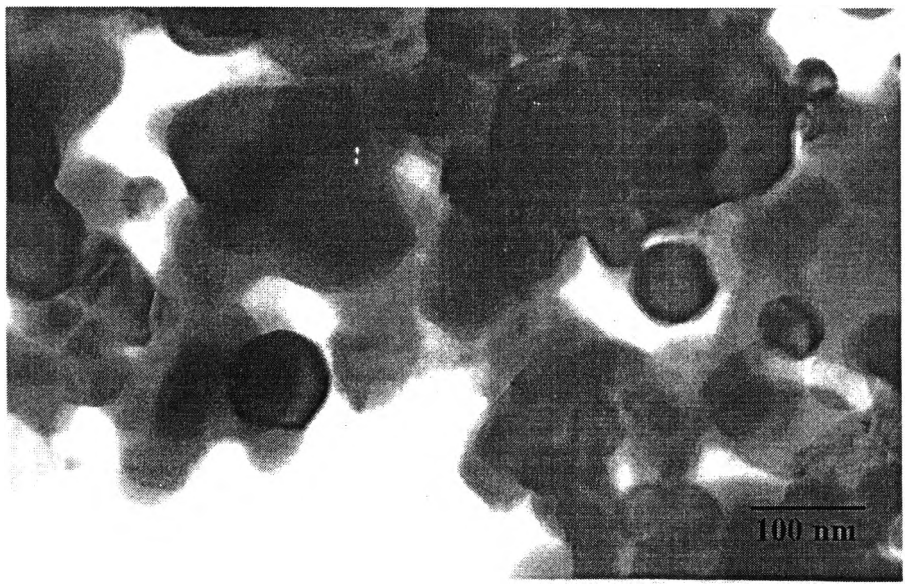

Figure 5.35(b) TEM photograph of the product at Zn/Al=1.00 synthesized in 1-butanol after calcination at 1100°C.

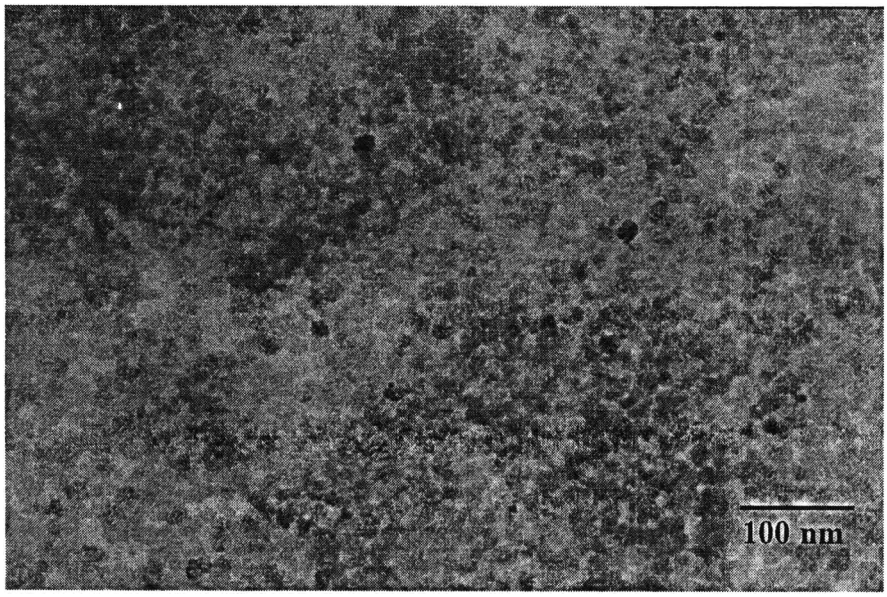

Figure 5.35(c) TEM photograph of the product at starting Zn/Al=0.50 synthesized in 1-butanol.

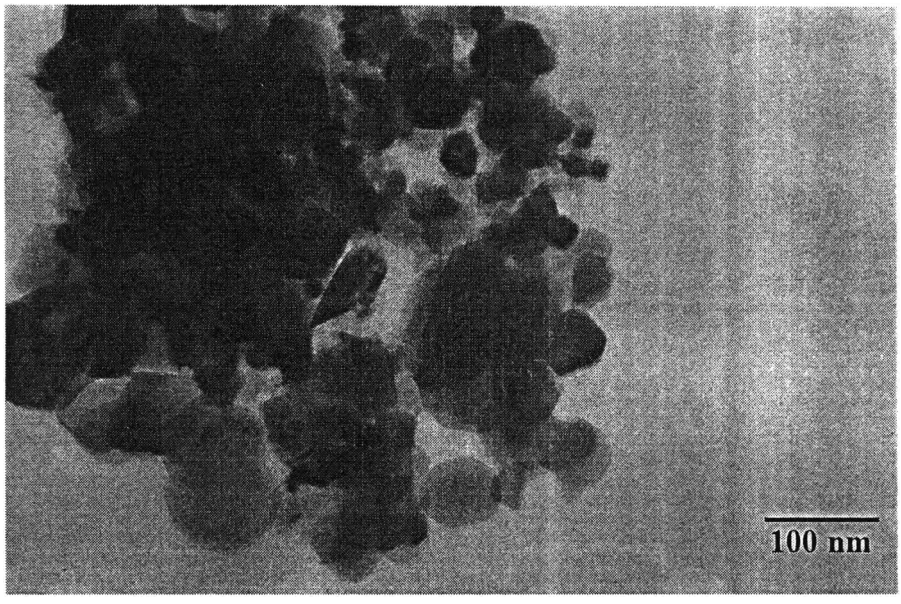

Figure 5.35(d) TEM photograph of the product at Zn/Al=0.50 synthesized in 1-butanol calcination at 1100°C.

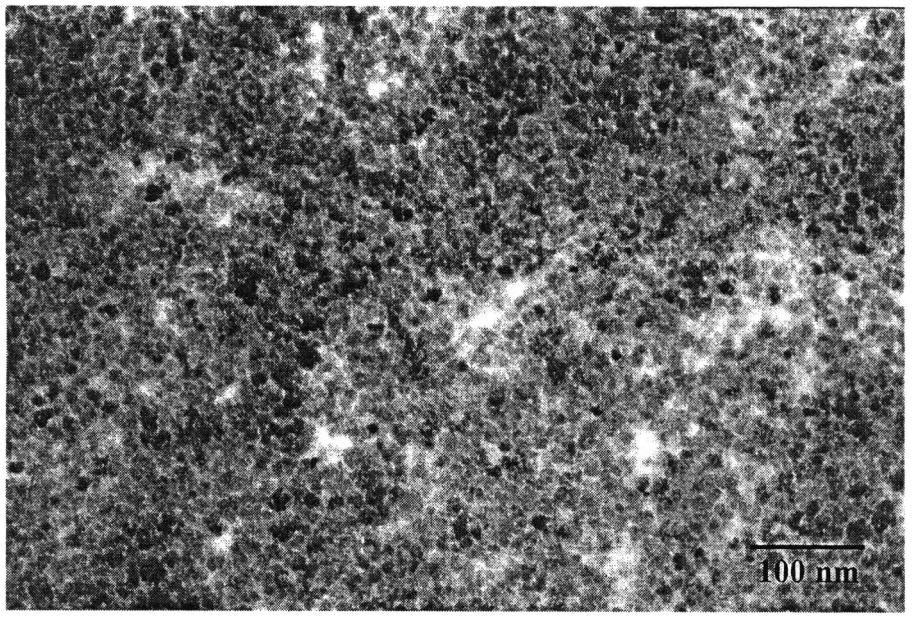

Figure 5.35(e) TEM photograph of the product at Zn/Al = 0.33 synthesized in 1-butanol

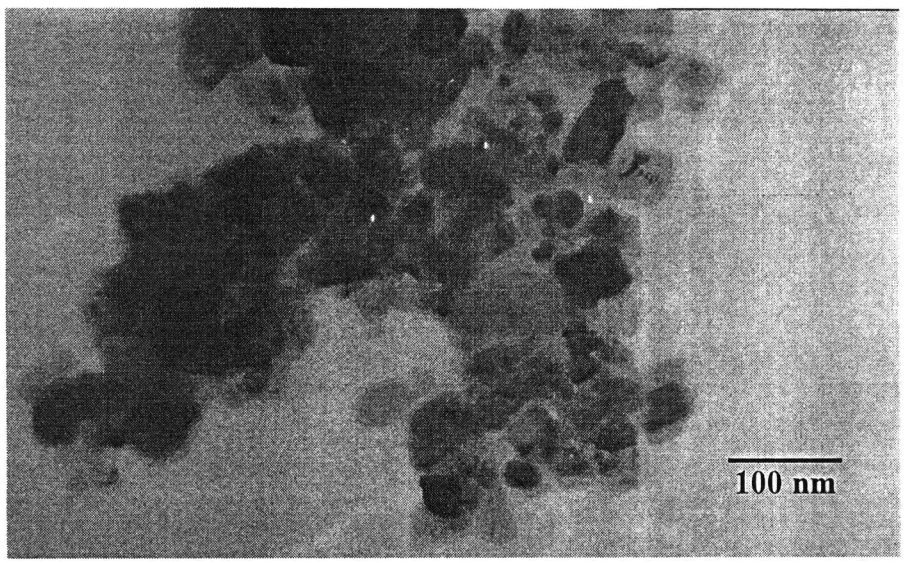

Figure 5.35(f) TEM photograph of the product at Zn/Al = 0.33 synthesized in 1-butanol after calcination at 1100°C.

Table 5.7 BET surface area and crystallite size of the products synthesized by 1-butanol and the samples calcined at various temperatures.

Charged Zn/Al ratio	S_{BET}[a](m^2/g)				d[b] (nm)				d[c] (nm)			
	as-syn	600°C	800°C	1100°C	as-syn	600°C	800°C	1100°C	as-syn	600°C	800°C	1100°C
0.33	176.31	106.16	42.17	20.06	10.89	13.62	28.41	72.82	10.99	13.33	28.33	73.15
0.50	139.51	60.83	30.14	11.18	8.27	11.99	38.97	152.25	8.33	12.15	38.33	152.33
1.00	210.87	50.02	32.45	6.86	8.42	15.97	34.26	418.41	8.67	16.33	34.67	419.15

[a]BET surface area.

[b]Crystallite size of the products calculated from Scherer equation using KCl as an internal standard

[c]Crystallite size of the products from TEM photograph.

Table 5.8 Chemical compositions of the as-synthesized products in various solvents

Starting Zn/Ga or Zn/Al ratio	Zn/Ga or Zn/Al of the as-synthesized products in various solvent[a]			
	toluene	1-butanol	2-propanol	1,4-butanediol
Zn/Ga = 0.33	-	0.311	0.325	0.323
Zn/Ga = 0.50	-	0.493	0.486	0.489
Zn/Ga = 1.00	-	0.987	0.982	0.991
Zn/Al = 0.33	0.318	0.327	0.325	0.328
Zn/Al = 0.50	0.498	0.493	0.487	0.489
Zn/Al = 1.00	0.954	0.968	0.953	0.971

[a] Zn/Ga or Zn/Al of the as-synthesized products obtained from XRF analysis.

5.3 Effect of the formation of spinel on the physical properties and the thermal stability of the products

As described in section 5.1 and 5.2, The products prepared in each organic solvent have different properties and thermal stability. It shows that their properties and thermal stability can be controlled by the formation of spinel crystal (type of organic solvent) besides reaction condition and structure of starting material. Therefore, the explanation about the mechanism of the formation of spinel crystal was required to clarify the occurred phenomena.

In the synthesizing of zinc gallate,the reaction of zinc acetate and gallium acetylacetonate in 1,4-butanediol at 300°C (glycothermal reaction) yielded nanocrystalline products having the crystallite sizes in the range of 7 to 15 nm. Under glycothermal conditions, zinc acetate and gallium acetylcetonatewere easily converted to glycoxides. Thermal decomposition of glycoxide molecules proceeded by intra molecular participation of the remaining hydroxyl group of the glycol moiety, yielding $-Zn-O^-$ and $=Ga-O^-$ anions. The nucleophilic attack of these gallate and zincate ions, and crystallization of zinc gallate took place. Finally, yielding the spinel zinc gallate which the amount of gallium and zinc in the structure depended on the amount of gallium acetylacetonate and zinc acetate used as the starting materials. In the case of the large amount of gallium acetylacetonate, the cyrstallized products were composed of the large amount of gallium in the structure. On the other hand, small amount of gallium acetylacetonate the spinel structure had the small amount of gallium. The mechanism of zinc acetate and gallium acetylacetonate in 1,4-butanediol can be depicted as follow:

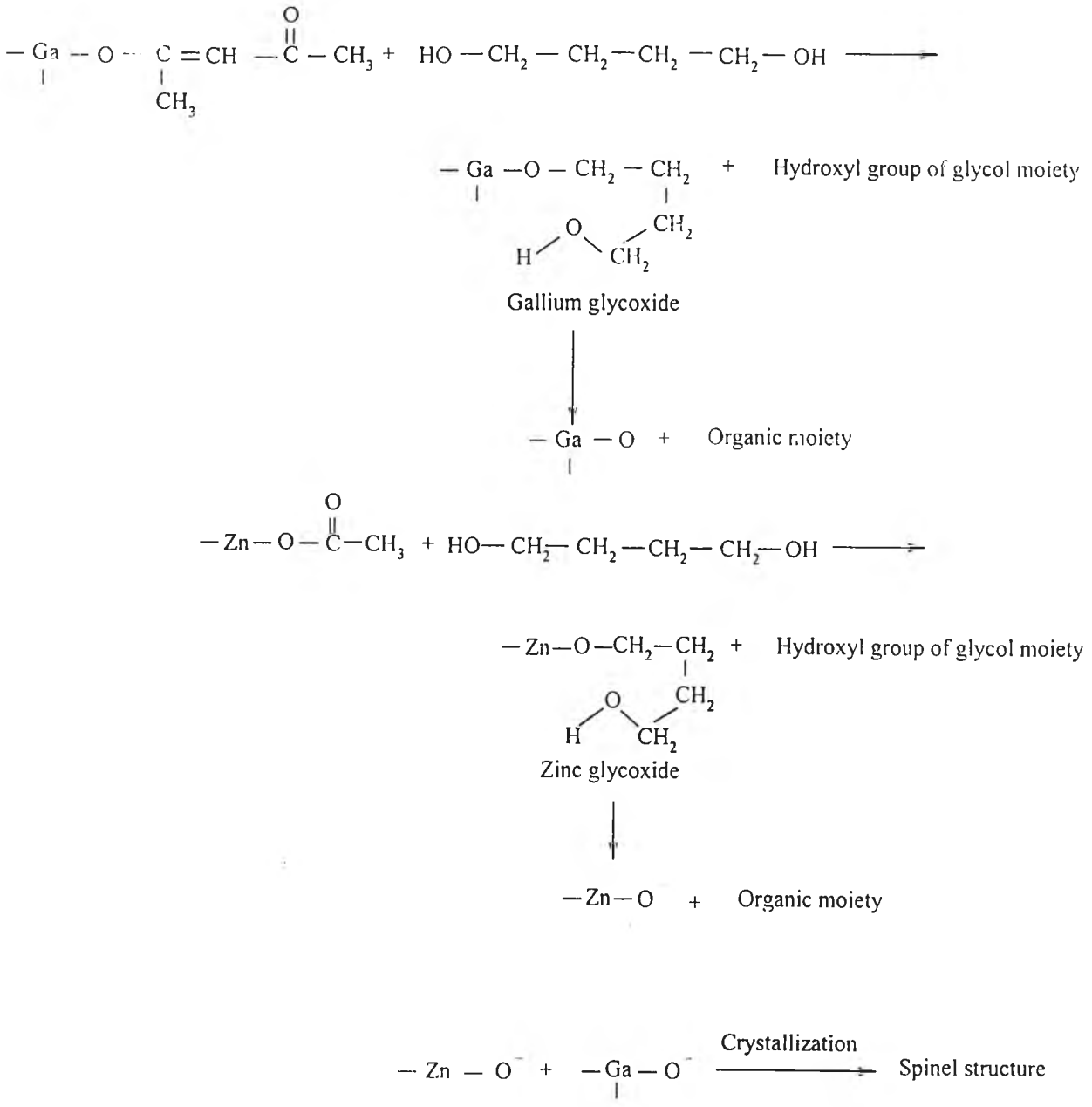

Figure 5.36 Mechanism of glycothermal reaction for the spinel zinc gallate formation

Similarly, the synthesizing of zinc aluminate the mechanism of zinc acetate and aluminium isopropoxide in 1,4-butanediol can be depicted as follow:

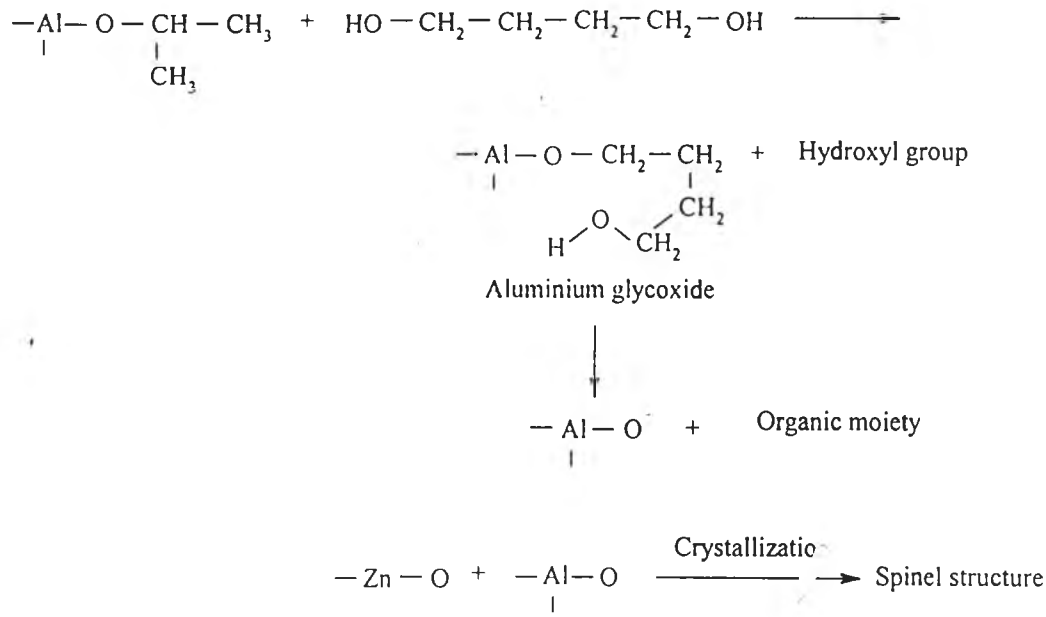

Figure 5.37 Mechanism of glycothermal reaction for the spinel zinc aluminate formation

Under inert organic solvent conditions, toluene, thermal decomposition of gallium acetylacetonate did not occur, yielding a $\equiv Ga\text{-}O^-$ anion. So the nucleophilic attack of the gallate ion on zincate ion and crystallization did not take place. Finally, zinc gallate was not yielded. However, thermal decomposition of aluminium isopropoxide occurred under the same condition yielded a $\equiv Al\text{-}O^-$ anion. The nucleophilic attack of the aluminate ion on zincate ion and crystallization took place, finally yielding the spinel zinc aluminate. The thermal decomposition mechanism of aluminium isopropoxide in toluene can be depicted as follow:

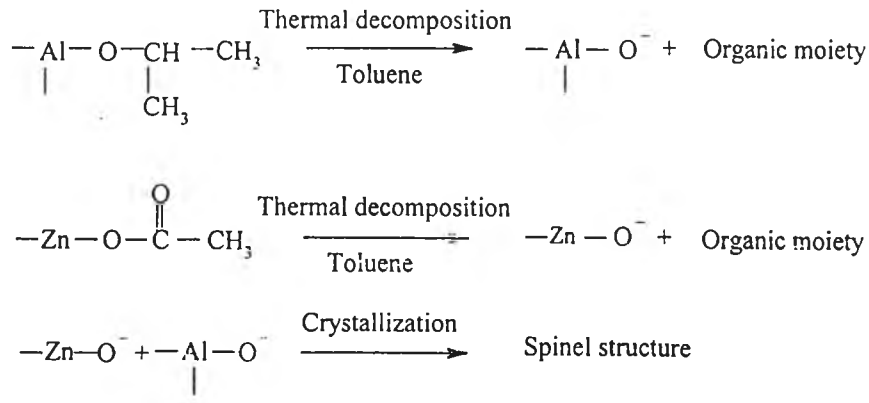

Figure 5.38 Mechanism of reaction in toluene for the spinel zinc aluminate formation.

Under THyCA conditions, thermal decompostion of gallium acetyl acetonate in 2-propanol occurred , yielding a =Ga-O$^-$ anion. Crystallization of spinel phase occurred, while 2-propanol dehydrated to be water and gallium acetylacetonate was hydrolyzed, yielding a =Ga-OH neucliophilic attacked on –ZnOH and crystallization of spinel phase took place, finally yielding the spinel zinc gallate. The mechanism of this reaction can be depicted as follow:

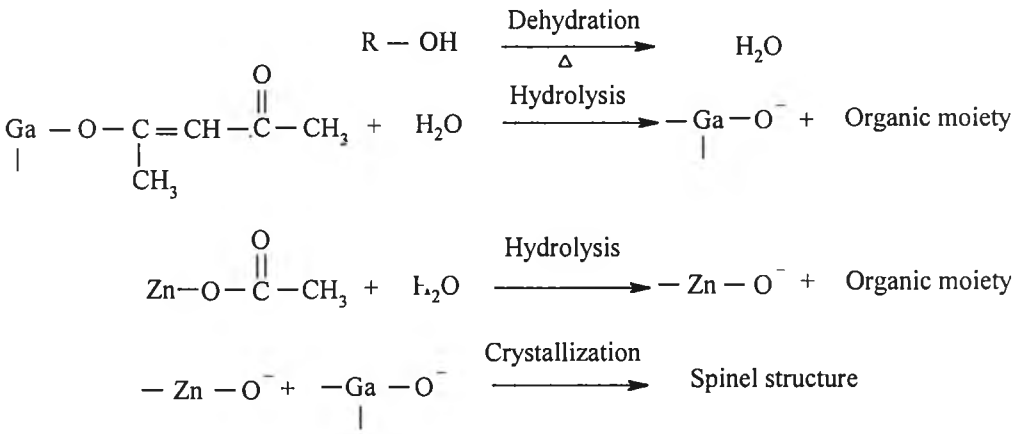

Figure 5.39 Mechanism of THyCA reaction for the spinel zinc gallate formation.

The reaction in 2-propanol of aluminium isopropoxide took place similarly. The mechanism of this reaction can be depicted as follow:

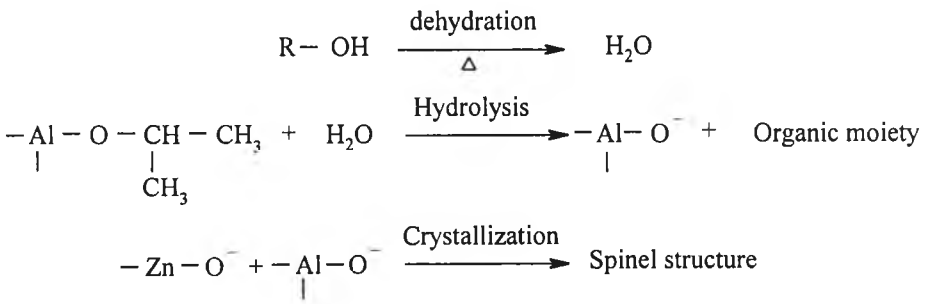

Figure 5.40 Mechanism of THyCA reaction of the spinel zinc aluminate formation

As described in previous section, the products of zinc gallate and zinc aluminate at starting Zn/Ga and Zn/Al ratios equal to 0.33 and 1.00 (nonstoichiometric ratios) were contaminated by another phase such as ZnO, Ga_2O_3, Al_2O_3, etc. In figure 5.42 to 5.44 shown the relation between thermal stability and crystallite size of products at various starting Zn/Ga and Zn/Al ratios.

In this work, thermal stability was defined as:

$$\text{thermal stability} = \frac{\text{BET surface area at any calcination at any temperature (BET)}}{\text{BET surface area of as-synthesized samples } (BET_0)}$$

Inoue et al. found that the type of organic solvent effects on thermal stability of metal oxide but in this work found that it did not effect on thermal stability of metal oxide.

In Figure 5.41, the data of the samples at Zn/Ga and Zn/Al equal to 0.50 synthesized in various solvents were plotted as the relation between log BET/BET_0 and log $T(K)/\sqrt{d_c(nm)}$; calined temperature(K)/√as-synthesized crystallite size (nm), are shown. From this figure, found that the thermal stability of the products was not depended on type of organic solvent. Additionally, it was shown that thermal stability of zinc aluminate is better than zinc gallate in the range of calcination temperature used. At higher calcination temperature zinc gallate tends to have greater thermal stability than zinc aluminate. And thermal stability of zinc gallate and zinc aluminate strongly depended on the crystallite size of them. Conversely, the rate of thermal stability decreasing of zinc aluminate is higher than that of zinc gallate. So, the thermal stability of zinc aluminate is more sensitive to the decreasing of the crystallite size than zinc gallate. However, organic solvents influenced on the crystallite sizes of the zinc gallate and zinc aluminate products. For the samples at nonstoichiometric starting Zn/Ga and Zn/Al ratios (0.33 and 1.00), this relation was not linear as the result of the contamination of the other phases (figure 5.42 and 5.43). Additionally, it was found that the second metal (Ga or Al) influence on the thermal stability of

double oxide differently. Finally, the presence of the second metal could encourage the thermal stability of metal oxide.

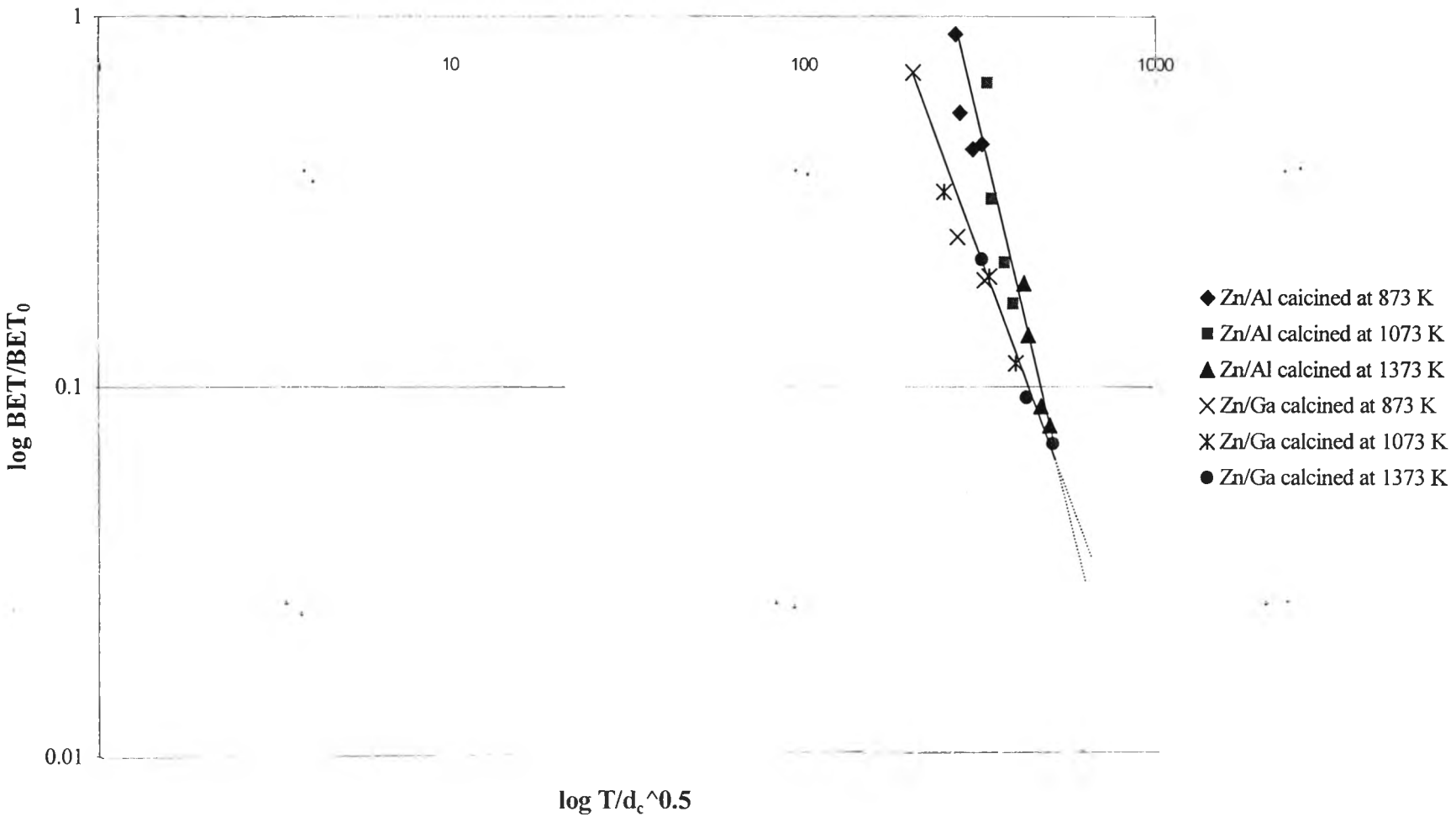

Figure 5.41 The relation between log BET/BET$_0$ and log T/d$_c$^0.5 of zinc gallate and zinc aluminate calcined at various temperatures.

Table 5.10. The thermal stability data for the relation in Figure 5.41

For zinc aluminate at starting Zn/Al = 0.50.

Solvent	d_c(nm)	873/d_c^0.5	BET/BET_0	1073/d_c^0.5	BET/BET_0	1373/d_c^0.5	BET/BET_0
toluene	7.35	322.011	0.452	395.78	0.1672	506.44	0.07843
1-butanol	8.27	303.572	0.436	373.12	0.2160	477.44	0.08828
2-propanol	10.43	270.316	0.891	332.24	0.6576	425.136	0.18977
1,4-butanediol	9.82	278.585	0.547	342.41	0.3210	438.142	0.13737

For zinc gallate at starting Zn/Ga = 0.50.

Solvent	d_c(nm)	873/d_c^0.5	BET/BET_0	1073/d_c^0.5	BET/BET_0	1373/d_c^0.5	BET/BET_0
1-butanol	7.08	328.0935	0.19321	403.258	0.11529	516.005	0.07021
2-propanol	10.02	275.7912	0.25329	338.974	0.19804	433.747	0.09331
1,4-butanediol	18.13	205.029	0.70210	252.000	0.33470	322.457	0.22052

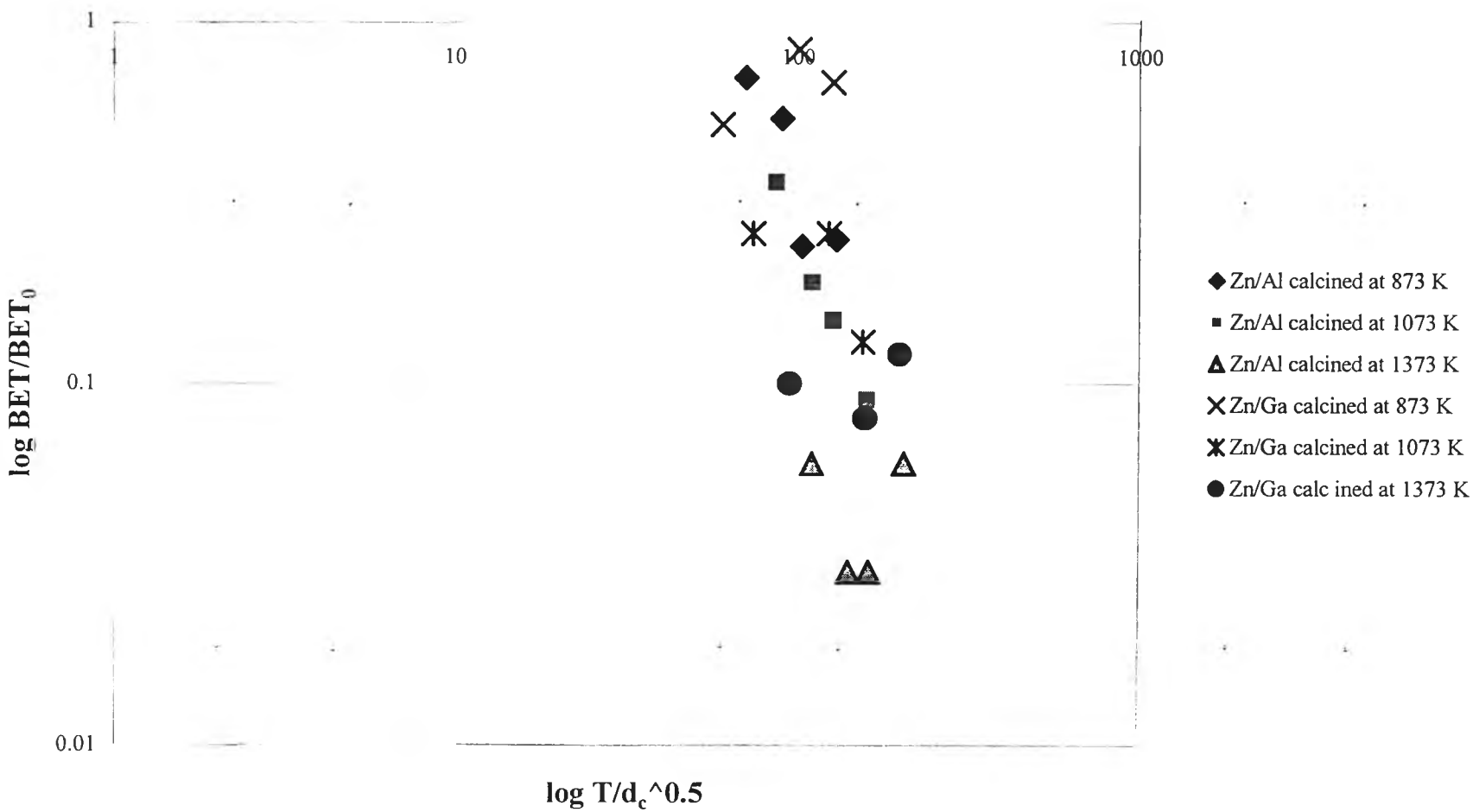

Figure 5.42 The relation between log BET/BET$_0$ and log T/d$_c$^0.5 of the products at starting Zn/Ga and Zn/Al = 1.00 calcined at various temperatures.

Table 5.11. The thermal stability data of the relation in Figure5.42

For zinc aluminate at starting Zn/Al = 1.00.

Solvent	d_c(nm)	873/d_c^0.5	BET/BET_0	1073/d_c^0.5	BET/BET_0	1373/d_c^0.5	BET/BET_0
toluene	6.67	130.8852	0.25	160.870	0.09	205.847	0.06
1-butanol	8.42	103.6821	0.24	127.435	0.15	163.064	0.03
2-propanol	9.67	90.2792	0.54	110.962	0.19	141.986	0.03
1,4-butanediol	12.36	70.6311	0.70	86.812	0.36	111.084	0.06

For zinc gallate at starting Zn/Ga = 1.00.

Solvent	d_c(nm)	873/d_c^0.5	BET/BET_0	1073/d_c^0.5	BET/BET_0	1373/d_c^0.5	BET/BET_0
1-butanol	6.87	127.0742	0.68	156.1863	0.13	199.854	0.12
2-propanol	8.65	100.9249	0.84	124.0462	0.26	158.728	0.08
1,4-butanediol	14.42	60.5409	0.52	74.4105	0.26	95.215	0.10

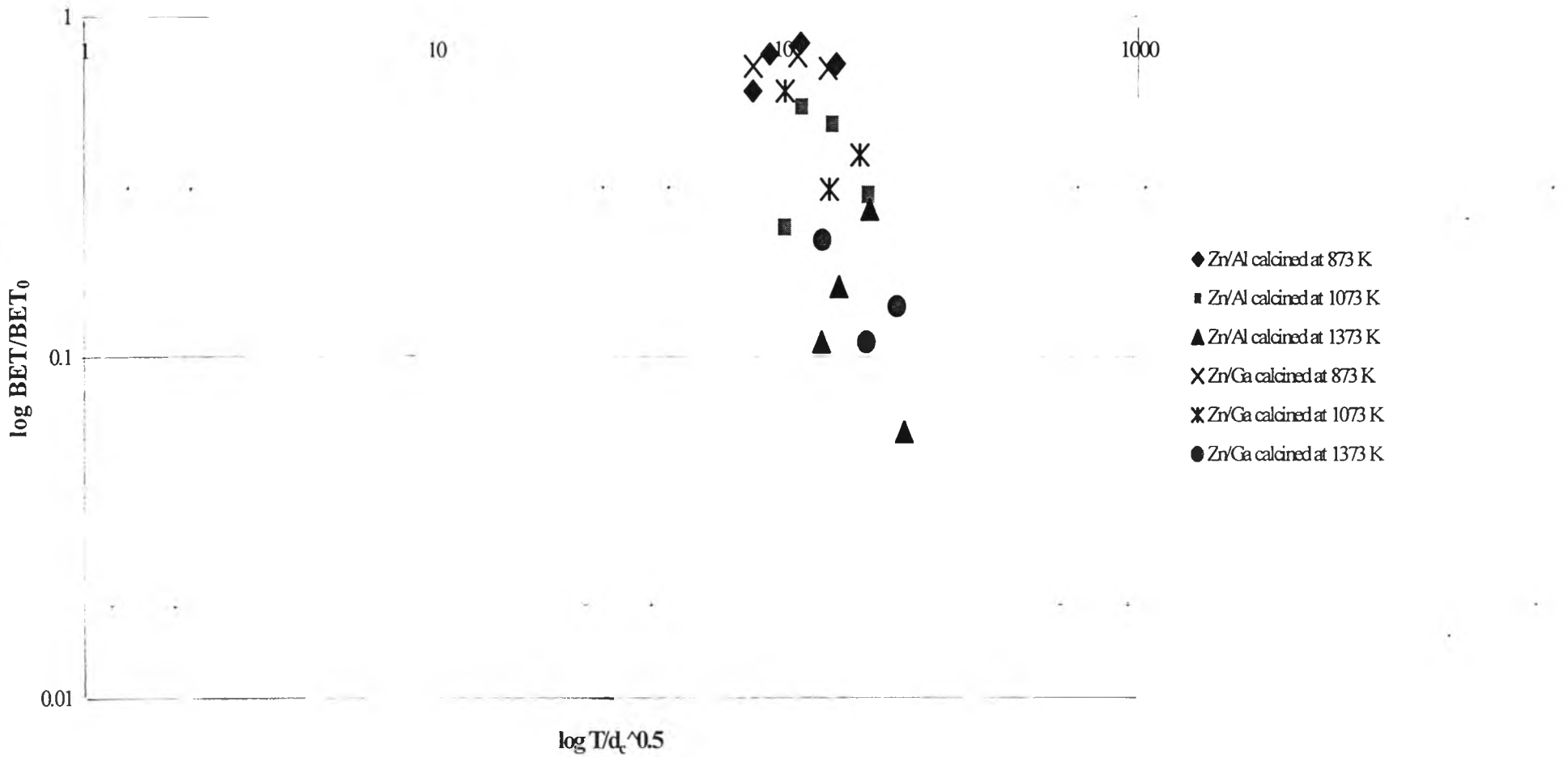

Figure 5.43 The relation between log BET/BET$_0$ and log T/d$_c$^0.5 of the products at starting Zn/Ga and Zn/Al = 0.33 calcined at various temperatures.

Table 5.12. The thermal stability data of the relation in Figure 5.43

For zinc aluminate at starting Zn/Al = 0.33.

Solvent	d_c(nm)	873/d_c^0.5	BET/BET_0	1073/d_c^0.5	BET/BET_0	1373/d_c^0.5	BET/BET_0
toluene	6.33	137.915	0.72	169.510	0.30	216.904	0.06
1-butanol	10.89	80.165	0.60	98.531	0.24	126.079	0.11
2-propanol	9.75	89.538	0.77	110.051	0.54	140.821	0.16
1,4-butanediol	7.98	109.398	0.83	134.461	0.48	172.055	0.27

For zinc gallate at starting Zn/Ga = 0.33.

Solvent	d_c(nm)	873/d_c^0.5	BET/BET_0	1073/d_c^0.5	BET/BET_0	1373/d_c^0.5	BET/BET_0
1-butanol	6.67	130.885	0.70	160.871	0.39	205.847	0.14
2-propanol	8.13	107.380	0.76	131.980	0.31	168.881	0.11
1,4-butanediol	10.86	80.388	0.71	98.803	0.60	126.427	0.22