

Microwave Synthesis of Nanocrystalline Yttria

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Abstract—Nanocrystalline yttrium oxide (yttria) single phase has been processed using a microwave and conventional assisted sol gel process using nitride precursors. Single phase yttria was achieved at 700°C using microwave heating after half hour, while conventional heating required higher times. The prepared yttria powder was characterized using X-ray diffraction, scanning electron microscope (SEM), and transmission electron microscope (TEM). The microwave method was found to yield yttria particles that slightly smaller that of conventional one under similar condition of calcination (temperature and time). The activation energy for crystal growth were determined for both conventional and microwave calcinations. Also, substantial morphological differences were observed between the yttria particles and their agglomerates produced by the different processing methods.

Keywords—Microwave, Sol-gel, Yttria, Activation Energy.

I. INTRODUCTION

YTTRIA has attractive properties like high chemical and thermal stability, and optical transparency over a wide wavelength region which makes it a great candidate for optical and solar applications. Other applications are high temperature chemical-resistant substrates, crucibles for melting reactive metals and nozzles for jet-casting molten, rare-earth-iron magnetic alloys [1]. There are several methods reported for the processing of yttria ceramic powders. They include precipitation, hydrothermal, co-precipitation, glycothermal treatment, electro-spray-pyrolysis and sol-gel processing [2]. Each one of these methods has their merits and demerits. To achieve the desired phase purity and particle size, the process of conventional solid state reaction usually needs lengthy high temperature treatment (>1600°C) and extensive ball milling, which generally introduces additional impurities and defects. All these processes require a relatively long duration of calcination step involving temperatures in excess of 900°C. Therefore wet chemical processes such as hydroxide coprecipitation, alkoxide- and glycothermal based routes, as well as combustion synthesis, have been used [3] for producing yttria as a fine powder. The alkoxide approach is restricted due to the rather difficult synthesis and the limited commercial availability of various metal alkoxides. Due to the explosive character of the combustion process, the particle size cannot be controlled easily. Microwave assisted combustion synthesis of ceramic oxides is fundamentally different from the conventional combustion in which heat is generated within the reactants material itself by absorbing the microwaves in the microwave oven. Microwaves interact with the matter from bulk to the surface and the heat generation is

governed by the rapid kinetics of the dipole moments of the molecules. The application of microwave heating irradiation in the preparation of nanocrystalline advanced ceramics can be seen in many recent works [4].

In this work, a microwave assisted synthesis of single phase yttria using a citrate gel process involving nitrates of Y is described. Both microwave and conventional heating are adopted. The activation energy for crystal growth was determined for both conventional and microwave calcinations.

II. EXPERIMENTAL PROCEDURES

Nitrates of yttrium ($Y(NO_3)_3 \cdot 6H_2O$) were dissolved in an aqueous solution of citric acid (99.9%) purity, Aldrich Chemicals Ltd., UK). The prepared solution was 2 M of citric acid and 0.2 molar in yttrium nitrate. This solution was heated at 80 °C under continuous stirring to obtain a gel. The latter was dried at 110°C for 24 h and the resultant powder was heated to 220 for two hours to remove the nitride. The powder was then calcinated using conventional and microwave heating between 500–1000°C in a silica crucible using a muffle furnace and a 2.45 GHz multimode microwave cavity, respectively. The sample temperature was measured using a shielded, Pt sheathed K type thermocouple. The microwave and conventionally prepared powders were characterized using XRD phase-composition analysis. Mean crystallite size was calculated using X-ray half peak broadening and the Scherrer equation. The particle size and morphology were investigated using scanning electron microscope (SEM) and transmission electron microscope (TEM). The synthesis procedure is summarized in Fig. 1.

III. RESULTS AND DISCUSSION

A. Crystal Formation

The XRD pattern for the conventional and microwave synthesized powders for yttria is shown in Fig. 2 and Fig. 3, respectively. Fig. 2 shows the XRD pattern for conventional heating while Fig. 3 is for microwave heating. The calcination temperature ranges from 600C to 1000C. The calcination time ranged from 30 min to 12 hours for the conventional heating while the microwave heating ranged from 15 min. to 1 hour. It can be noticed that the formation of crystallized yttria is present at 700C. At a temperature bellow 700C, the transformation to yttria was not complete. Soaking time of 30 min was enough to produce a homogenous yttria in the compound. Using XRD pattern, the crystal size of yttria was calculated via Scherrer equation. Table 1 presents the crystal size of the yttria powder under both conventional and microwave calcination. It can be seen

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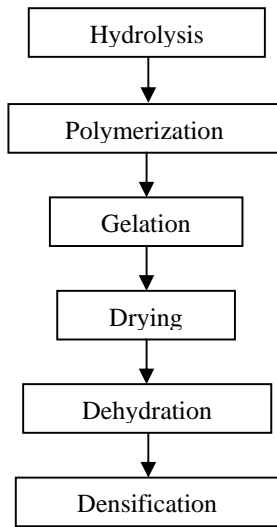


Fig.1 The synthesis procedure for sol-gel processing of Yttria

that the crystal size of the powder increase with both temperature and time. It is also observed that the crystal size of the conventional calcination gives larger crystals compared to microwave ones. The effect of temperature on the crystal size is more pronounced than the effect of calcination time. Crystal size of the yttria powder ranges from 12.56 to 36.1nm for the temperature range used (700-1000°C) in the case of conventional calcinations, while the microwave calcination gave rise to crystal size ranging from 12.04 to 25.91nm for the temperature range (700-900°C).

Fig. 4 shows the scanning electron microscope (SEM) images for both conventionally and microwave prepared yttria powders. Both powders were heavily agglomerated. The transmission electron microscope (TEM) was used to characterize the microwave prepared powders. Fig. 5 shows the TEM image of microwave prepared powder at 800°C for 60 minutes. The crystal size of the TEM image ranges between 15-18nm which matches well with the XRD crystallite size.

A. Crystal growth of nanocrystalline yttria

The nanocrystalline yttria powders was prepared using conventional and microwave calcination. The powders were calcinated at different temperature ranging from 700-1000°C. Fig. 6 shows the effect of temperature on the crystal size of the yttria powders. Fig. 6a shows the grain growth in the conventional calcination while Fig. 6b shows the grain growth in the microwave calcination. The grain growth in the conventional calcination was 12.56 to 36.1nm which is about 200% increase in the crystal size for the temperature range used (700-1000°C) while the microwave calcination gave rise to crystal size ranging from 12.04 to 25.91nm which is about 100% increase in the crystal size for the temperature range (700-900°C). The effect of time on the grain growth of yttria powders is presented on Fig. 7. Fig. 7a represents the

grain growth for conventional heating while Fig. 7b represents the grain growth for microwave heating. It can be noticed that the effect of heating time on the grain growth are less significant compared to the effect of temperature as discussed earlier. In the conventional heating the grain size changes from 12.8 to 17.49 nm, which is about 40% increase in the crystal size. In the microwave heating, the grain growth was from 16.83 to 18.5nm which is about 10% increase in the crystal size. It should be noted here that the effect of time was done in two different temperatures. For the conventional heating, the effect of time was investigated at 700°C while for microwave heating the effect of time was investigated at 800°C.

The activation energy for the crystallite growth can be determined using the rate equation. The phenomenological kinetic grain-growth equation states:

$$G^n - G_o^n = K_o t e^{-\frac{Q}{RT}} \quad (1)$$

where G is the crystal size at the desired temperature, G_o is the initial crystal size, n is the grain size exponent, K_o is constant, t is time, Q is the activation energy, R is the gas constant, and T is temperature in degree Kelvin. Since the powder was initially in the amorphous form, G_o is considered zero and Eq. (1) reduce to:

$$G^n = K_o t e^{-\frac{Q}{RT}} \quad (2)$$

The investigation of the activation energy of yttria was conducted in two different steps. The first step is the study of the grain growth at constant temperature to determine n . For conventional heating the temperature selected was 700°C while for microwave heating the temperature selected was 800°C. For the investigation of crystal growth at constant temperature, the exponential term in eq. (2) becomes constant and can be multiplied with the K_o constant to produce the following equation:

$$G^n = At \quad (3)$$

where A is the new constant resulting from the multiplication of K_o and the exponential term in eq.(2).

Taking the logarithm of eq. (3) will result in the following equation:

$$\log G = \frac{1}{n}(\log A + \log t) \quad (4)$$

The relation between grain growth and time in the double-logarithmic scale, for both conventional and microwave calcinations, can be drawn as shown in Fig. 8 where the slope of the straight line will be equal to $1/n$. Fig. 8a represents the conventional heating while Fig. 8b represents the microwave heating. The grain size exponent, n , can be determined from the slope of the straight line in Fig. 8. The resulting grain size exponent, n , are 10.2 for the conventional calcination and 13.9 for the microwave calcination. The difference in the grain size exponent can be attributed to the limited time used in microwave calcination.

The second step of investigation is the effect of temperature on the grain growth at constant time. At constant time, eq. (2) can be rewritten in the following form:

$$G^n = B e^{-\frac{Q}{RT}} \quad (5)$$

where B is the multiplication of K_o and time, t .

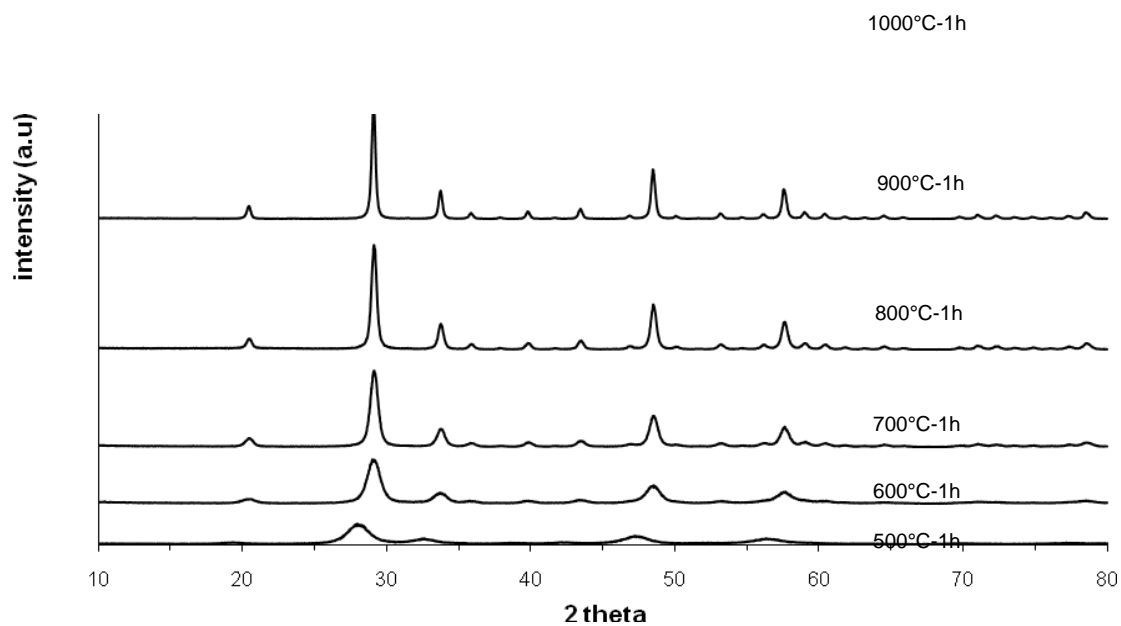


Fig. 2. XRD patterns of the conventionally calcinated yttria at different temperature

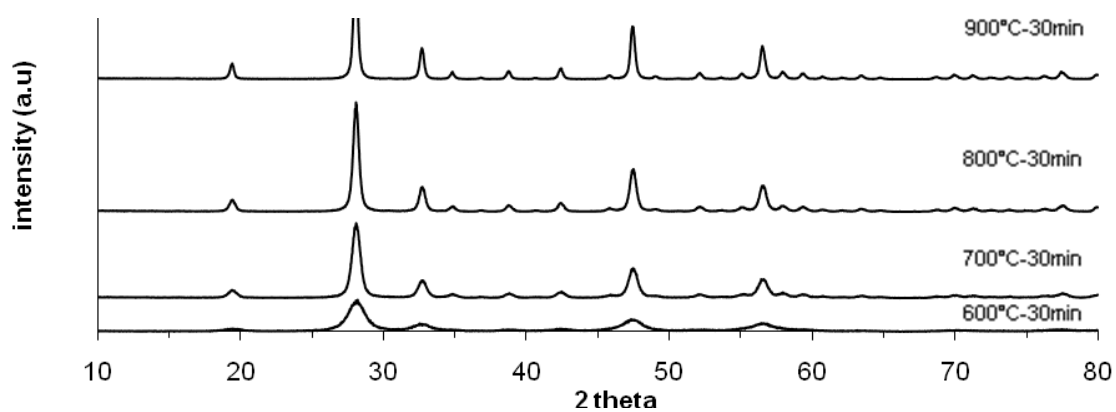
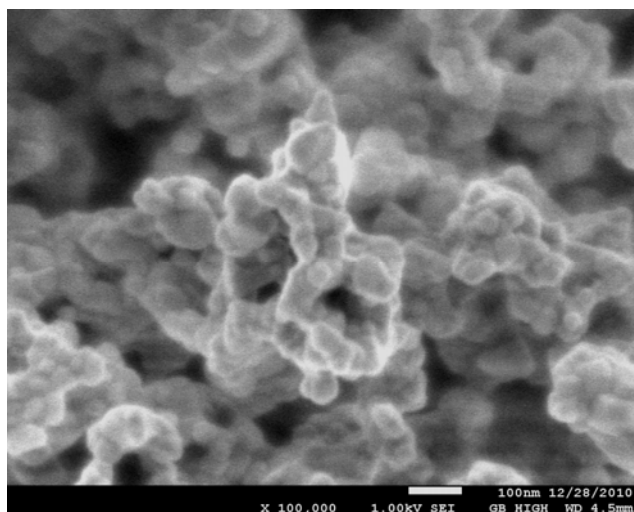


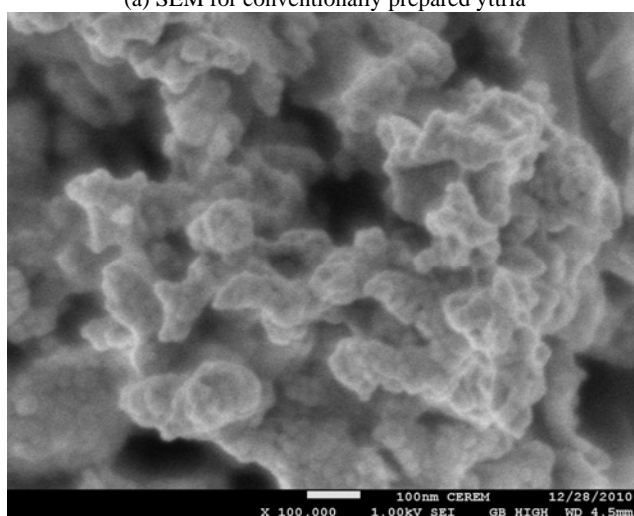
Fig. 3. XRD patterns of the Microwave calcinated yttria at different temperature

TABLE I

CRYSTAL SIZE OF YITTRIA POWDERS. (A) CONVENTIONAL CALCINATION, (B) MICROWAVE CALCINATION					
(A) CONVENTIONAL CALCINATION			(B) MICROWAVE CALCINATION		
Temp	Time	Crystal Size (nm)	Temp	Time	Crystal Size (nm)
600	30 min	7.06	600	30 min	7.06
	1h	7.4		1h	7.4
	3h	8.19		3h	8.19
	6h	9.18		6h	9.18
700	30 min	12.58	700	30 min	12.58
	1h	12.68		1h	12.68
	3h	14.43		3h	14.43
	6h	14.62		6h	14.62
	12h	17.49		12h	17.4
800	30min	19.55	800	30min	19.55
900	30min	28.71	900	30min	28.71
1000	30min	36.1	1000	30min	36.1



(a) SEM for conventionally prepared yttria



(b) SEM for microwave prepared yttria

Fig. 4. SEM images of conventionally and microwave yttria powders at 950°C for 30min calcination time. (a) Conventional, (b) Microwave

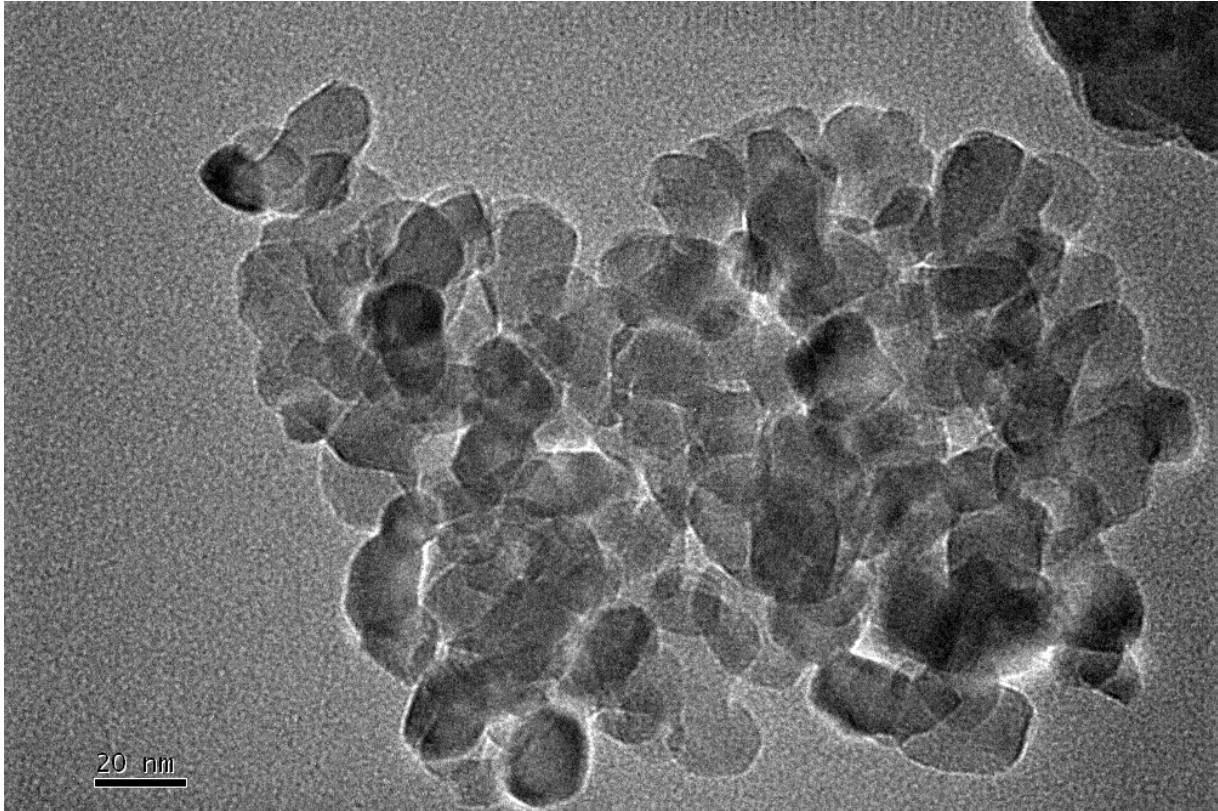


Fig. 5 TEM image of microwave prepared powders at 800°C for 60min.

Taking natural the logarithm of eq. (5) leads to the following:

$$\ln G = \frac{1}{n} \ln B - \frac{Q}{nR} \left(\frac{1}{T} \right) \quad (6)$$

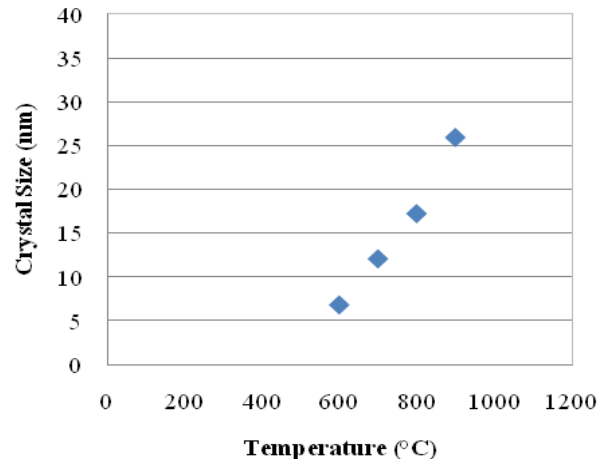
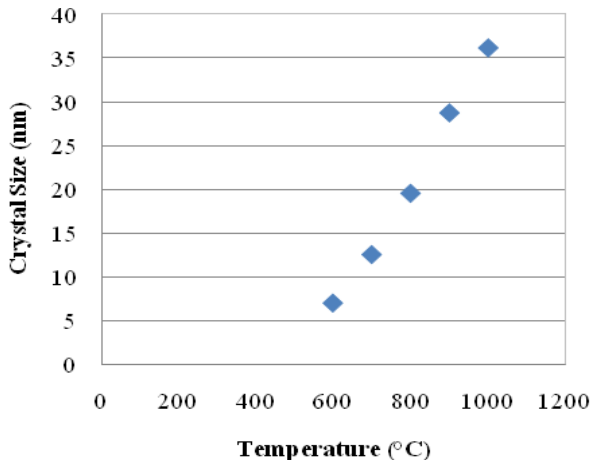
The relation between grain growth and temperature in the semi-logarithmic form for both conventional and microwave calcination can be drawn as shown in Fig. 9 where the slope of the straight line will be equal to $Q/2.3nR$. Fig. 9a represents the conventional heating while Fig.(9b) represents the microwave heating. The activation energy, Q , can be determined from the slope of the straight line in Fig. 9 to be:

$$Q = \text{slope} \times 2.3nR \quad (7)$$

The resulting activation energy can be determined as 398 kJmol^{-1} for conventional calcination and 519 kJmol^{-1} for microwave calcination. The difference in the value of the activation energy can be attributed to the difference in the grain size exponent reported earlier. However, the present results have a good agreement with the reported activation energy in the literature which was 410 kJmol^{-1} as reported by Wang et. al [5] and 418 kJmol^{-1} which was reported by Chen and Chen[6]. The controlling mechanism for the grain growth in the present study is believed to be grain boundary diffusion of yttrium [5].

IV. CONCLUSION

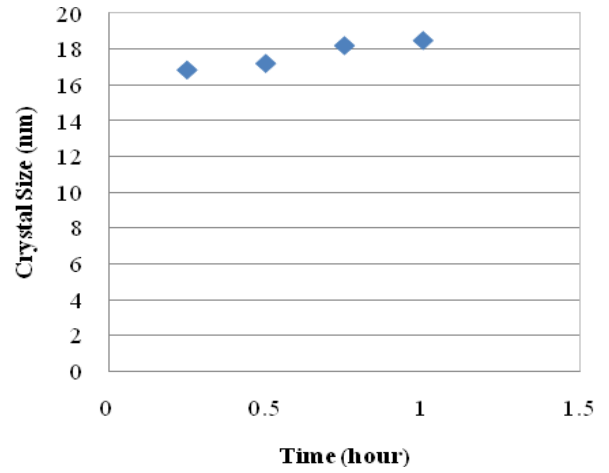
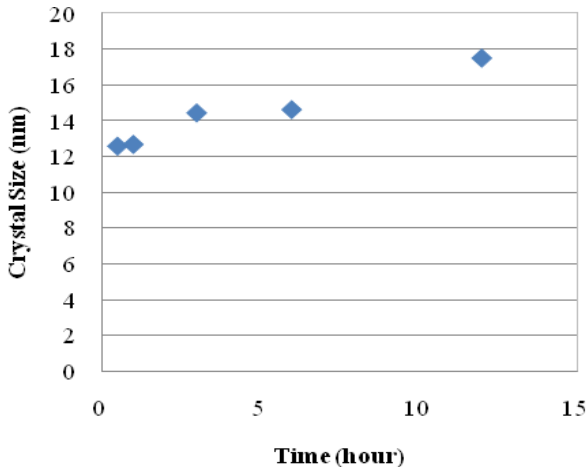
Single phase, nanocrystalline Yttria powder has been synthesized using a microwave assisted citrate gel process at temperatures as low as 700°C. The resulted grain growth was compared to conventional calcination. The microwave calcination gave slightly lower grain size as compared to the conventional calcinations at similar condition. Both conventional and microwave calcinations gave similar grain growth behavior. The microwave calcination gave a higher activation energy due to the difference in grain size exponent which was due to the limited heating time range. The controlling mechanism for the grain growth in the present study is believed to be grain boundary diffusion of yttrium. The major advantage for the microwave calcination is the speed of the process and the low energy consumed during the calcinations process.



(a) Conventional

(b) microwave

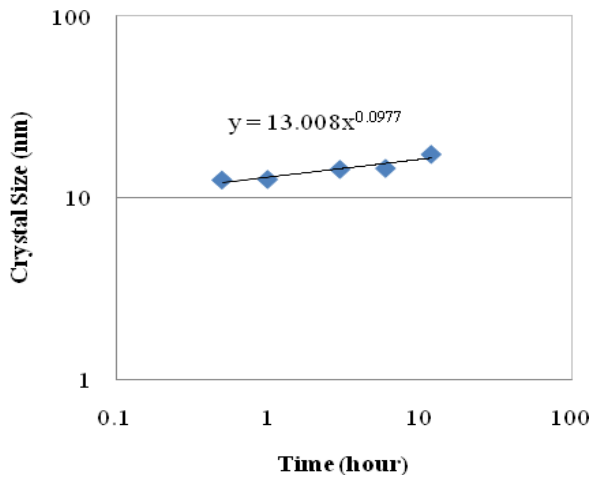
Fig. 6 the effect of temperature in the crystal growth for conventionally and microwave prepared powders for 30min heating cycle. (a) conventional, (b) microwave



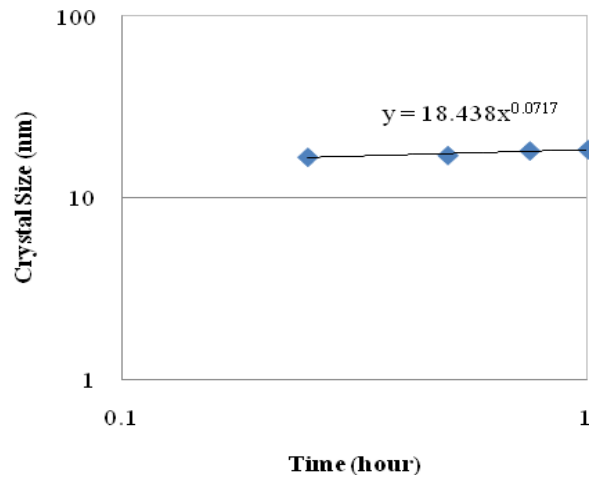
(a) conventional calcination at 700°C

(b) Microwave calcination at 800°C

Fig. 7 the effect of time in the crystal growth for conventionally and microwave prepared. (a) conventional at a temperature of 700 C, (b) microwave at a temperature of 800 C

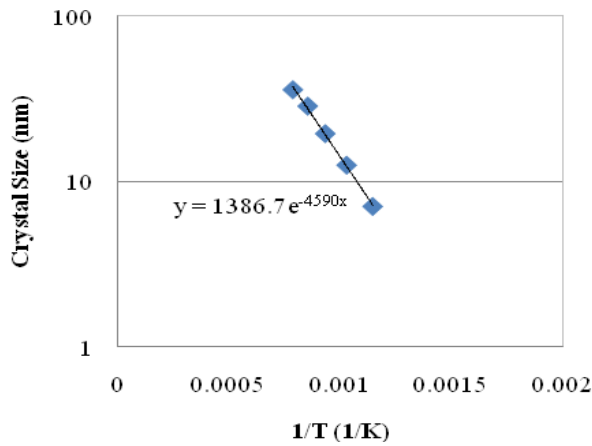


(a) Conventional calcination at 700°C

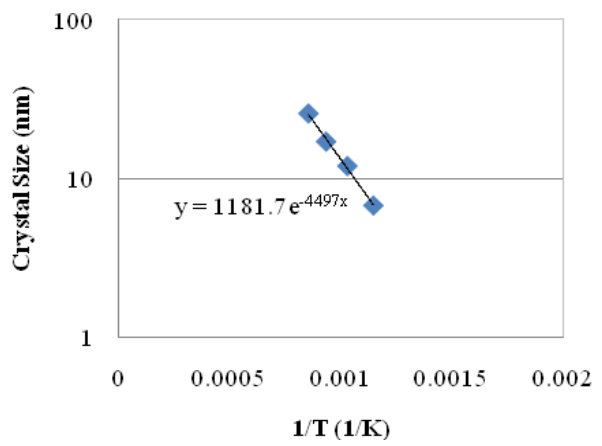


(b) Microwave calcination at 800°C

Fig. 8 The effect of time on crystal growth in the double logarithmic form for the conventionally and microwave calcination of yttria powders. (a) Conventional calcination, (b) Microwave calcination.



(a) Conventional calcination



(b) Microwave calcination

Fig. 9 The effect of temperature on crystal growth in the double logarithmic form for the conventionally and microwave calcination of yttria powders. (a) Conventional calcination, (b) Microwave calcination.

REFERENCES

[1] B. Smith, "An approach to graphs of linear forms (Unpublished work style)," unpublished.

[2] E. H. Miller, "A note on reflector arrays (Periodical style—Accepted for publication)," *IEEE Trans. Antennas Propagat.*, to be published.

[3] J. Wang, "Fundamentals of erbium-doped fiber amplifiers arrays (Periodical style—Submitted for publication)," *IEEE J. Quantum Electron.*, submitted for publication.

[4] C. J. Kaufman, Rocky Mountain Research Lab., Boulder, CO, private communication, May 1995.

[5] Y. Yorozu, M. Hirano, K. Oka, and Y. Tagawa, "Electron spectroscopy studies on magneto-optical media and plastic substrate interfaces (Translation Journals style)," *IEEE Transl. J. Magn.Jpn.*, vol. 2, Aug. 1987, pp. 740–741 [*Dig. 9th Annu. Conf. Magnetics Japan*, 1982, p. 301].

[6] M. Young, *The Technical Writers Handbook*. Mill Valley, CA: University Science, 1989.

[7] J. U. Duncombe, "Infrared navigation—Part I: An assessment of feasibility (Periodical style)," *IEEE Trans. Electron Devices*, vol. ED-11, pp. 34–39, Jan. 1959.

[8] S. Chen, B. Mulgrew, and P. M. Grant, "A clustering technique for digital communications channel equalization using radial basis function networks," *IEEE Trans. Neural Networks*, vol. 4, pp. 570–578, July 1993.

[9] R. W. Lucky, "Automatic equalization for digital communication," *Bell Syst. Tech. J.*, vol. 44, no. 4, pp. 547–588, Apr. 1965.

[10] S. P. Bingulac, "On the compatibility of adaptive controllers (Published Conference Proceedings style)," in *Proc. 4th Annu. Allerton Conf. Circuits and Systems Theory*, New York, 1994, pp. 8–16.

[11] G. R. Faulhaber, "Design of service systems with priority reservation," in *Conf. Rec. 1995 IEEE Int. Conf. Communications*, pp. 3–8.

[12] W. D. Doyle, "Magnetization reversal in films with biaxial anisotropy," in *1987 Proc. INTERMAG Conf.*, pp. 2.2-1–2.2-6.

