Synthesis of Y_2O_3 Nanoparticles by Modified Transient Morphology Method

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Abstract. Yttrium oxide nano-powder has been successfully synthesized by a modified transient morphology. In the first step, a foamy structure was produced by combustion synthesis using yttrium nitrate and glycine. This was followed by the addition of sulfate ions and calcination at 1100 °C for 4 h. The phase composition of the products after combustion synthesis and sulfate addition was analyzed by XRD. The XRD pattern shows Y_2O_3 single phase after calcination. The crystallite size XRD was estimated from the broadening of XRD peaks, using Scherrer's formula. Williamson – Hall plotting method estimates the strain and the mean nano crystallite size. The sulfated powders were characterized by transmission electron microscopy (TEM), too. The TEM images confirm the nanometric size of the particles in the range of 40-100nm.

Keywords: Yttrium oxide; nano-powder; modified transient morphology; combustion synthesis

1. Introduction

Yttrium sesquioxide, Y_2O_3, has recently attracted much attention because of several particularly interesting physical properties, such as its crystallographic stability up to $2325°C$ (melting point of Y_2O_3 is $2450°C$), high mechanical strength, high thermal conductivity ($0.13 Wcm^{-1} K^{-1}$), large optical band gap (~5.5 eV) [1], a relatively high dielectric constant in the range 14–18, a rather high refractive index near n = 2 which is well suited for waveguide applications, and very good protective behavior as a coating in severe reactive environments [2]. Y_2O_3 with cubic symmetry is one of the important oxide hosts for the solid state lasers, as well as for infrared ceramics [3]. Eu-doped Y_2O_3 is a well known red phosphor. It has been proposed as a replacement for SiO_2 for dielectric films in electronic devices because of high dielectric strength (k=18) and low leakage current [4].

Yttrium oxide also possesses superior resistance to aggressive chemical attack by molten metals, salts, slag and glass at high temperatures. It is used for coating crucibles and moulds that handle highly reactive molten metals like uranium, titanium, chromium, beryllium and their alloys. A thin coating of Y_2O_3 is claimed to prevent corrosion of the substrate material by molten uranium and other reactive metals. It is also seen to be fairly stable with graphite up to $1600°C$ [5].

In this work, Y_2O_3 nano particles are synthesized by modified transient morphology method. This method is attracted much attention because of convenient process and needing simple instrument. The transient morphology method is based on combustion synthesis and introduced by Mouzon and his co-workers for synthesize of Y_2O_3 nano particles [6]. In this research, the transient morphology method was modified and become more economic because all processing steps are done simply without a fully automated batch reactor and do not need to expensive instruments.

2. Experimental

All chemicals used in this work were Merck products of analytical grade and used without further purification. In the first step, a foamy structure was produced by combustion synthesis using yttrium nitrate

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and glycine. This was followed by the addition of sulfate ions and calcination at 1100°C for 4 h. The prepared powders were characterized by X-ray powder diffraction (XRD) and transmission electron microscopy (TEM). Y_2O_3 nano powder synthesized by the transient morphology method is summarized in a flow chart shown in Fig. 1.

2.1. Foamy Structure Synthesis

Yttrium nitrate ($Y(NO_3)_3$, 3.5 N solution) and glycine ($C_2H_5O_2N$) were used as the oxidizer, the fuel, respectively. A fuel to nitrate ratio of 0.32 was employed. In a typical run, 2.49 g of glycine was added to 10 ml of the yttrium nitrate solution and mixed for 30 min, in a Pyrex beaker. Then the Pyrex beaker placed in a pre-heated furnace at 500 °C in air. Boiling occurs first and was then followed by smoldering with evolution of a large amount of brown red gases, expelling most of the final product out of the beaker. After heating for 13 h, the final product consists of flakes with white color and showing extremely low density.
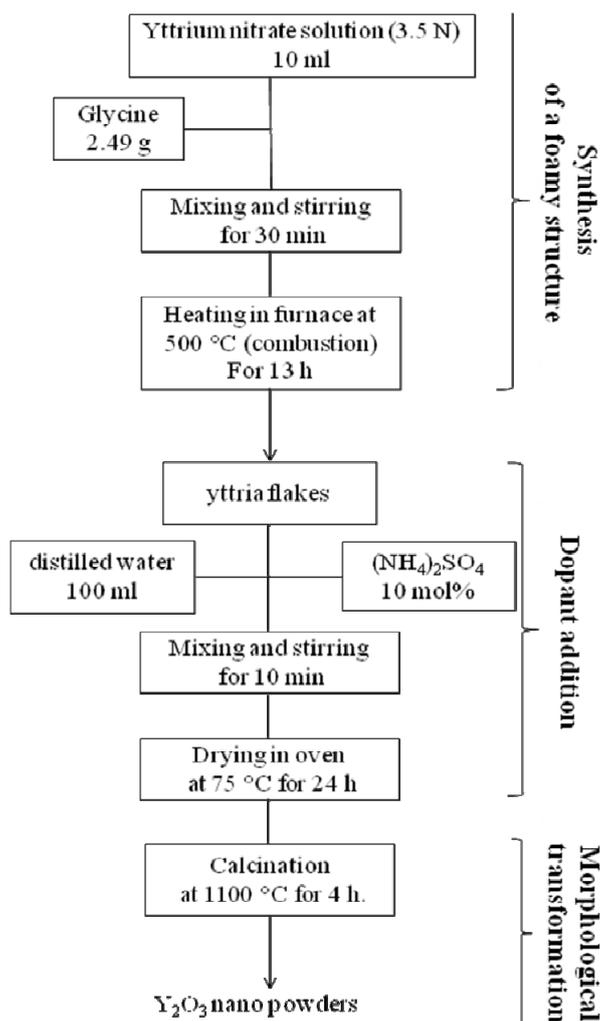

Fig. 1: The flow chart of preparation of Y_2O_3 nano particles by transient morphology method.

2.2. Sulfate Addition

In case of sulfate ion addition, 0.9811g of the collected yttria flakes were dispersed together with 10 mol% of $(NH_4)_2SO_4$ on the yttrium ion basis in 100 ml distilled water on a magnetic stirring plate. The volume occupied by the flakes in the beaker was far larger than 100 ml. After 10 min stirring, the mixture was dried in an oven at 75 °C for 24 h.

2.3. Calcination

After drying, the cake fell off very easily and could be removed from the beaker by a spoon. The resulting powder were placed in an alumina crucible and calcined in a furnace with at 1100°C during 4 h.

2.4. Characterization

The X-ray diffraction (XRD) patterns of the powders after sulfate addition and after calcination were recorded by the D8 Advance Bruker system using CuKα (λ=0.154056 nm) radiation with 2θ in the range 10-80°. Transmission electron microscopy (TEM) micrographs were recorded by LEO system (model 912 AB) operating at 120kV. The required samples for TEM analysis was prepared by dispersing the Y_2O_3 nano powders in methanol using an ultrasound bath. A drop of this dispersed suspension was put onto 200-mesh carbon coated Cu grid and then dried in vacuum.

3. Results and Discussion

The phase composition of the products after combustion synthesis and sulfate addition was also analyzed by XRD. Fig. 2a shows the diffractogram of the corresponding powder after combustion synthesis. It can be noticed that the diffraction peaks that can be distinguished are fairly consistent with those of yttrium oxide [7], but the peak around 10° is characteristic of yttrium hydroxide or yttrium hydroxynitrate compounds. This confirms the fact that hydroxide groups have formed on the surface of the particles. The extent of hydroxylation is thought to be related to the slow drying rate at 75 °C, which has caused the powder to remain in water for a prolonged period. So calcination is required in any case to achieve the oxide phase and higher purity. After calcination at 1100 °C, pure yttrium oxide is obtained, as shown in Fig. 2b. The XRD peaks sharpened after calcination temperature, indicating crystallite growth. The XRD patterns show that the intensities of three basic peaks of the (2 2 2), (4 4 0) and (6 2 2) planes are more than of others peaks.
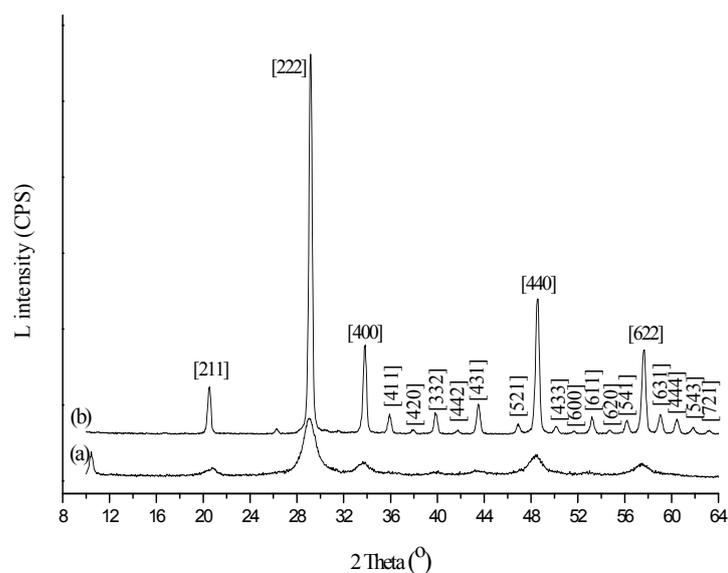

Fig. 2: X-ray diffractograms of the powder: (a) after combustion synthesis and sulfate addition (b) after calcination

Table 1 shows the XRD parameters and mean crystallite size of the Y_2O_3 nano particles in various crystalline orientations at different annealing temperatures. As seen in Table I, the width of the peaks decreases after calcination which refers to the growth of crystals size and construction of larger clusters.

The crystallite size XRD was estimated from the broadening of XRD peaks, using Scherrer's formula (1) [8]:

$$d_{XRD} = \frac{K\lambda}{\beta \cos\theta} \qquad (1)$$

Where θ is the Bragg angle of diffraction lines, K is a shape factor taken as 0.9, λ is the wavelength of incident X-rays (λ=0.154056 nm), and β is the full-width at half maximum (FWHM).

The presence of impurity in lattice structure changes lattice energy and causes the excess strain. The strain and the mean size of nano particles were calculated by using the Williamson – Hall formula Eqs. (2) based on the XRD patterns [9].

$$\beta \cos \theta = \frac{K\lambda}{\prec d \succ} + 2\varepsilon \sin \theta \tag{2}$$

Where ε is the strain and d is the mean size of crystallite. So if we plot βcosθ against 2sinθ it can be get a straight line with gradient ε and intercept Kλ/d (Fig. 3.)

Tab 1. The XRD Parameters and Crystalline Size in Different Crystallography Orientations

	hkl	2θ	Intensity	FWHM	d(obs)	D
		Deg	(cps)		Å	"Scherrer̓s formula"
						nm
Before Calcination						
	222	29.078	1231	1.174	3.0703	7
	440	48.381	503	1.117	1.87477	8
	622	57.449	350	1.228	1.60195	7
After Calcination						
	211	20.525	958	0.321	4.32401	25
	222	29.17	7533	0.325	3.05872	25
	400	33.807	1787	0.327	2.64923	25
	440	48.548	2704	0.358	1.87371	24
	622	57.631	1691	0.377	1.59815	24

The strain, determined from the slope, is 4.9×10^{-4} which shows removing organic additives. The mean value of nano crystallite is obtained 26nm. If the Scherrer's formula is used, the calculated value of the crystallite size changes depending upon the used peak. Large variation needs to be noted. This happens because peak broadening increases with the diffraction angle, and the effect of strain variance on the peak broadening is not considered. In comparison, the crystallite size by Williamson-Hall formula does not change depending upon peak positions.
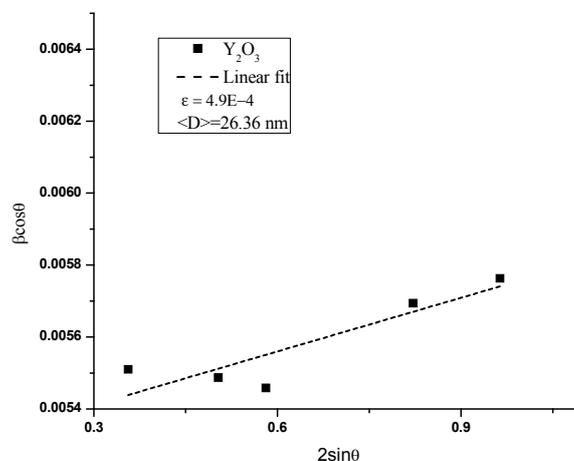

Fig.3: Williamson – Hall plot for the calculation of strain and the mean crystallite size

The TEM micrographs of the Y_2O_3 nano-powders are shown in Fig. (4). The TEM images confirm the nanometric size of the particles in the range of 40-100nm.

4. Conclusion

Yttrium oxide nano particles were synthesized successfully by simple and low costs modified transient morphology method. Characterization of powder after combustion synthesis by x-ray diffraction indicates the presence of yttrium hydroxide that after calcination at 1100 °C, all the impurity peaks are removed from the powders, and crystalline Y_2O_3 nano particles are formed. The mean size range of crystallites (by XRD patterns) was between 20 - 30nm. Williamson – Hall plotting method estimates the strain and the mean nano crystallite size 4.9×10^{-4} and 26nm respectively. The TEM image shows nano particles with size in the range of 40-100 nm.
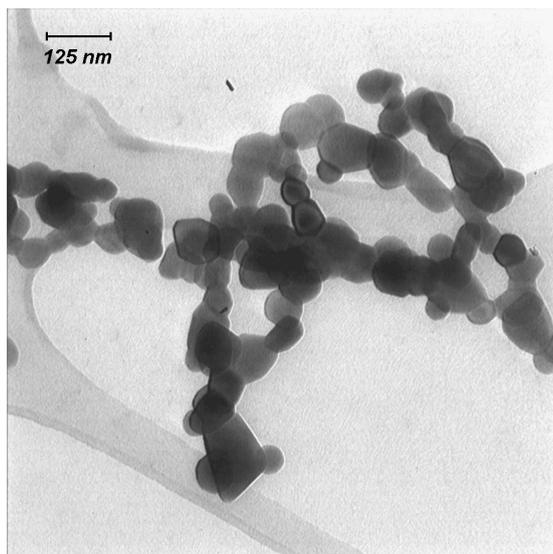

Fig.4: The TEM image of Y_2O_3 nano particles calcined at $1100^{o}C$

5. References

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