CHAPTER 3
SYNTHESIS PROCEDURE OF Y_2O_3:Gd NANOPARTICLES

3.1 Compounds

The precursor that was used in this experiment is yttrium nitrate hexahydrate, $Y(NO_3)_3.6H_2O$ (Kanto Chemical, Japan, 99.99%). This compound weight is 383.01 gram.mol^{-1} and has a melting point of 100 ^oC. It is odorless, colorless to pink crystalline solid and soluble in water, alcohol, ether, and nitric acid.

The second precursor that was used in this experiment is gadolinium nitrate hexahydrate, $Gd(NO_3)_3.6H_2O$ (Kanto Chemical, Japan, 99.95%). This compound weight is 451.36 gram.mol^{-1} and has a melting point of 91 ^oC. It is odorless, white crystalline solid and soluble only in water.

Polyethylene glycol (PEG) is also used as an inhibitor polymer which has melting point at 63 ^oC. PEG has $H(OCH_2CH_2)_nH$ cluster, where n is the amount of the chain of polymer. In this research, PEG which has molecular weight of 20000 was chosen because its non reactive nature with metallic ions in order to prevent agglomeration within nanoparticles. This polymer is also non corrosive in the presence of glass and soluble in water. Adding more PEG in the precursor might intensify the coating of the oxide particles with the carbonaceous materials. As a result, the size of oxide particles decreases when PEG content is increased.

3.2 Instruments

3.2.1 Programmable Electric Furnace

Heating was performed using programmable electric furnace and it is controlled by using digital program controller, KP1000 series, Chino Corporation, Japan.

The maximum temperature which can be reached by this instrument is 1200 ^oC. We also used the crushable alumina as the place of sample during the heating process. This instrument is provided at Physics of Electronic Material Research Group, Faculty Mathematics and Natural Sciences, Bandung Institute of Technology.

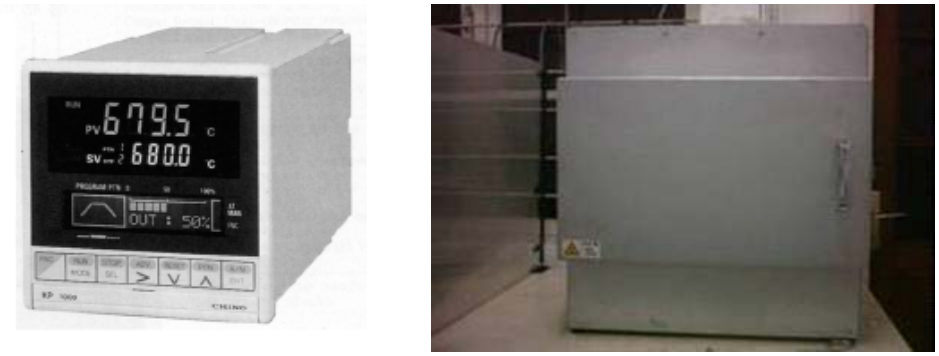

FIGURE 3.1 Digital program controller, KP 1000 series, Chino Corp (left) and heater (right)

3.2.2 Energy Dispersive X-Ray Analysis

EDX (Energy dispersive X-Ray Analysis) was used to detect the composition of nanoparticles. This technique is used in conjunction with SEM. The electron beam, which has 5-10 keV, hits the surface of conducting sample and lead to the emission of X-Ray from the material. The electron beam across the material is moved to acquire an image of each element in the sample. The detector, which is used in EDX, is the Lithium drifted Silicon (SiLi) detector, and it must be operated at liquid nitrogen temperature. The instrument is provided at Quaternary Laboratory, The Center of Geological Research and Development, Bandung.

3.2.3. Scanning Electron Micrograph

SEM (Scanning Electron Micrograph) was used to investigate the morphology of nanoparticles. This is a technique to study surface topography. A high energy (in this experiment we use 20 keV) electron beam is scanned along the surface. The incident electron causes low energy secondary electrons to be generated, and some escape from the surface. The secondary electrons, which emitted from the sample, are detected by a phosphor screen. This screen will glow and the intensify of light is measured with photomultiplier.

Size of nanoparticles was determined manually using vernier caliper. Several samples of nanoparticles (around 90 sample) were taken and subsequently analysize by using Microsoft Excel. The instrument is provided at Quartenary Laboratory, The Center of Research and Development Geology,Bandung.

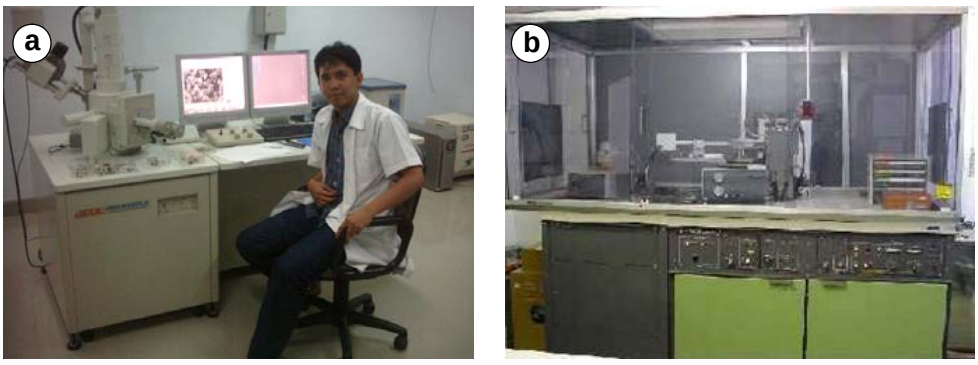

FIGURE 3.2 (a) Scanning Electron Micrograph equipment integrated with Energy Dispersive X-Ray Analysis equipment, and (b) X-Ray Diffraction equipment

3.2.4 X-Ray Diffraction

XRD (X-Ray Diffraction) was used to determine the crystallinity of nanopaticles. This method is based on Bragg's Law. By varying the angle θ, the Bragg's Law condition is satisfied by different d-spacing polycrystalline material. Plotting the angular positions and intensities of the resultant diffracted peaks of radiation produces a pattern, which is the characteristic of the sample. Structural, physical, and chemical information about the material investigated can be obtained based on the principle of X-ray diffraction. The instrument is provided at Mining Engineering Laboratory, Faculty of Earth Sciences and Mineral Technology, Bandung Institute of Technology.

A perfect crystal will extend in all directions to infinity, so we can say that no crystal is perfect due to its limited sizes. Such a deviation from perfect crystallinity will lead to the broadening of the diffraction peak. However, this type of peak's broadening is negligible when the crystallite size is larger than 200 nm. Crystallite size is a measure of the size of a coherently diffracting domain. Due to the presence of polycrystalline diffracting domain aggregates, crystallite size may not be the same thing as particle size.

Scherrer (1918) first observed that small crystallite size could give rise to peak broadening. He derived a well-known equation for relating the crystallite size to the peak's width, which is called the Scherrer formula [24].

The prediction of crystallite size Y_2O_3:Gd nanoparticle is determined from XRD pattern using Scherrer formula.

$$D = \frac{0.9\lambda}{B\cos\theta_B} \tag{3.1}$$

D = crystallite diameter

λ = the wavelength of X-Ray

B = the Bragg line/FWHM

θ_B = the Bragg angle

A full width at half maximum (FWHM) is an expression of the extent of a function, given by the difference between the two extreme values of the independent variable at which the dependent variable is equal to half of its maximum value. Microcal Origin 5.0 software is used to determine FWHM value by fitting the graphics using Lorentzian function and finally, FWHM and θ_B is obtained.

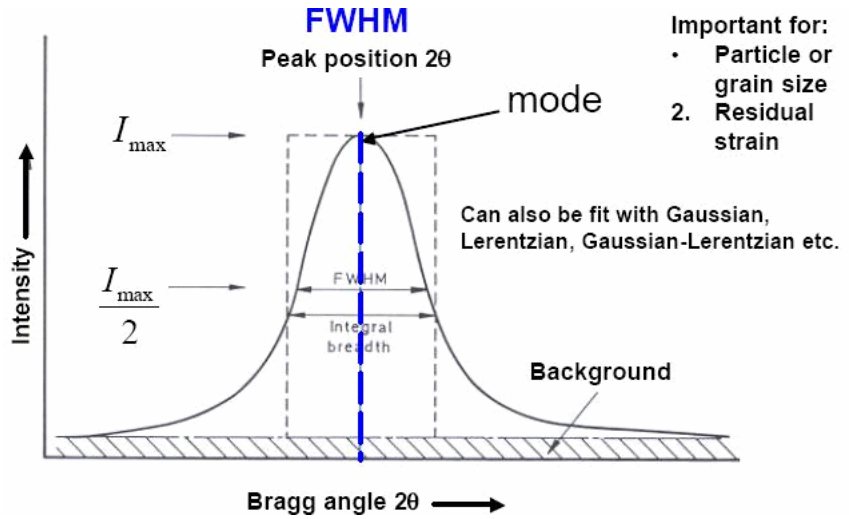

FIGURE 3.3 Expression of full width at half maximum (FWHM)

3.3 Experimental Method

Polymer heating process is a method for creating nanoparticles using continuous medium. Gadolinium doped yttrium oxide were produced by dissolving 3.83 g of yttrium nitrate hexahydrate and various quantities of gadolinium nitrate hexahydrate in 20 mL ultrapure water. This precursor was then stirred until a clear solution was obtained. Afterwards, 8 g polyethylene glycol is added to the precursor as an inhibitor polymer, followed by heating under stirring at 70 ^{o}C for several minutes to produce clear viscous precursor solution. This solution was heated at different temperatures and times. The variations in parameters including doping, temperature, and heating were done to obtain optimum nanoparticles quality which are determined by its nanometer dimension and high crystallinity.

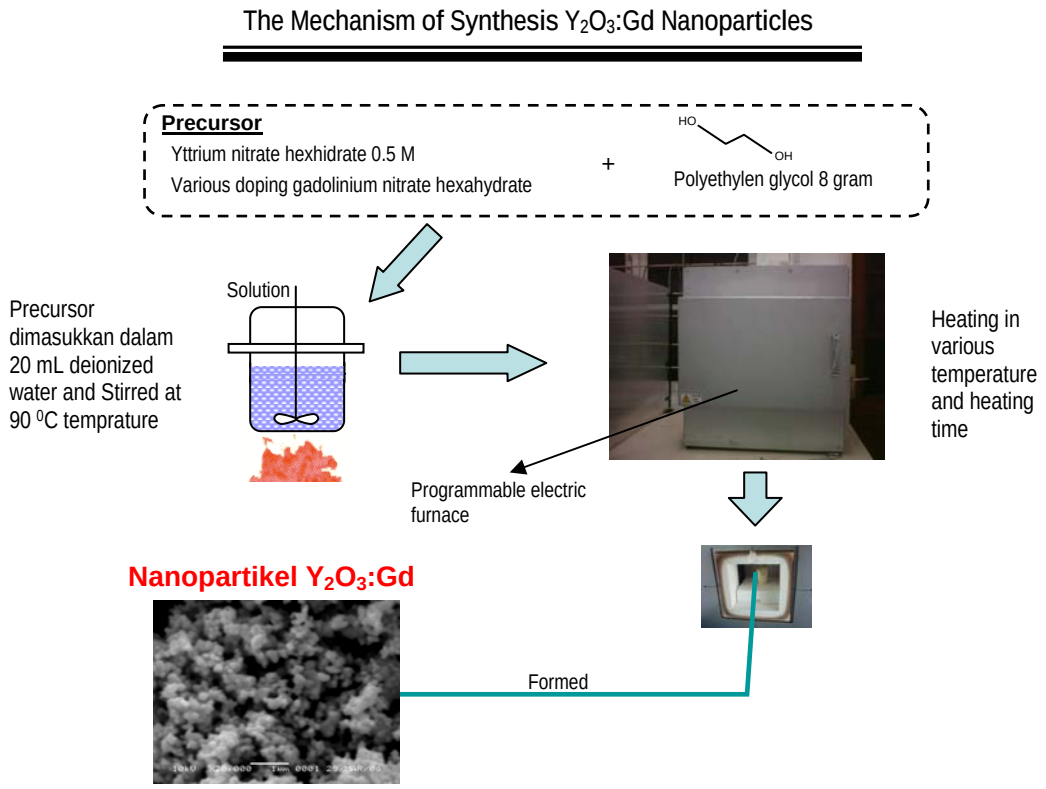

FIGURE 3.4 The mechanism of Y_2O_3:Gd nanoparticles' synthesis

3.4 Samples Variation

In this experiment, there were seven samples produced in variation of parameter. This is done to get the optimal synthesis of nanoparticles parameterization which is view from the smallness of particle size and the height of crystallinity. Samples variation includes the amount of gadolinium doping, the heating temperature, and the heating time. From the seven samples (see **TABLE 3.1**), the nanoparticles characteristic which obtain from EDX, SEM, and XRD characterization will be studied and analyzed.

TABLE 3.1 The variation of dopant fraction, heating temperature, and heating time for different samples.

SAMPLE	VARIOUS PARAMETER		
	Dopan Fraction Gd/Y (mol/mol)	**Heating Temperature (^oC)**	**Heating Time (min)**
S1	3%	800	30
S2	6%	800	30
S3	9%	800	30
S4	6%	600	30
S5	6%	1000	30
S6	6%	800	10
S7	6%	800	60

- *Constant parameter:*
  $Y(NO_3)_3.6H_2O$ = 3.83 gram
  Polyethylene glycol = 8 gram
  Distillated water = 20 ml

We will see the effect of adding dopant 3%, 6%, and 9% from sample S1, S2, and S3 respectively. We also see the effect of Heating Temperature 600 ^oC, 800 ^oC, and 1000 ^oC from sample S4, S2, and S5. Finally, we will see the effect of Heating Time 10 min, 30 min, and 60 min from S7, S2, and S6.