



YTTRIUM OXIDE AS AN ENGINEERING MATERIAL

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ABSTRACT

Yttrium oxide (Y₂O₃) is an insulating, air stable, non-toxic material. It exhibits different particle sizes ranging from micrometer to nanometer and surface morphology depending on preparation conditions. Rare earth doped yttrium oxide found numerous applications ranging from optoelectronic to bio-imaging. Primary aim of this review is to overview the literature on Y₂O₃ not only its particle size dependence and luminescence intensity with annealing time but also its different surface morphology with respect to different preparation methods. Here we also include its possible applications such as sensor, laser, fluorescence bioimaging (FBI), photoluminescence, cathodoluminescence and additives coating in MOS-FET devices. **Keywords:** RE doped Y₂O₃, Surface morphology, effect of annealing time and applications.

I. INTRODUCTION

Yttrium oxide (Y₂O₃) is an air-stable, solid substance white in color. It is used in the field of material sciences, to make phosphors by adding some fraction of rare earth doping that are used in imparting the orange to red color of the picture tubes in televisions due to good color purity, chemical and thermal stability. Yttrium oxide also used in field emission display (FED), vacuum fluorescent display (VFD), plasma display panel (PDP), Electroluminescence (EL), Cathodoluminescence (CL), Thermoluminescence (TL)[1], solar energy conversion devices, ultraviolet emitters and for

immunoassays and also for telecommunication[2,3]. All these applications demand single phase and compositionally uniform high purity powders with small (micron to nano) and uniform particle size for high resolution high luminous efficiency. Yttrium oxide also for telecommunication (photonic waveguide) due to its high band gap (5.72 eV), with a very high refractive index (1.8) and wide transmission range (280-8000 nm)[1,3,4]. Another major use of the yttrium oxide nanoparticles is in inorganic synthesis. Electronic configuration of Yttrium is - Kr 4d¹ 5s² and oxygen is - 1s² 2s² 2p⁴, and chemical composition of Yttrium is 78.7 % and that of oxygen is 21.1 % in Yttrium oxide. Density of yttrium oxide is 5.01 g/mL and its molecular weight is 225.81.

Yttrium oxide is mainly extracted from mineral Xenotime (YPO₄). It has an affinity for oxygen and sulphur and is used as an additive to stabilize zirconia and as a sintering aid in sailons and silicon nitrate. Yttrium oxide (Y₂O₃) is a very interesting material for potential applications because of its relatively high thermal stability, good transparency to infrared radiation, high permittivity (1-7), high melting point (2439 °C)[5].

In microelectronics, Y₂O₃ is a candidate to be a gatedielectric material. Compatibility with silicon it has large conduction band offset and valence band offset (2.3 and 2.2 eV, respectively). Therefore Y₂O₃ could be considered for a replacement of SiO₂ in transistors and memories. In addition, Y₂O₃ could be used as a buffer layer for ferroelectrics and superconductors because of its low lattice-mismatch with silicon. Y₂O₃ has also been

investigated for use as optical and protective coating layers due to a high melting point and refractive index. In addition, Y_2O_3 is a constituent of several more complex thin film materials. $YBa_2Cu_3O_{7-\delta}$ is a well-known high- T_c superconductor [6,7]. Y_2O_3 is found to be in cubic α - Y_2O_3 is monoclinic γ - Y_2O_3 phases and can be used for planar optical waveguide [8,9].

Here for comparative study we prepare three samples of Y_2O_3 with Eu^{3+} = 1mol % by precipitation method. The raw materials for the synthesis of $Y_2O_3:Eu^{3+}$ phosphor by different synthesis route are used as Y_2O_3 (99.99%) and Eu_2O_3 (99.99%). For detail study refer R.S. Ukare et al.[10]. The dry precipitated was kept for heating at $800^\circ C$ for different annealing time.

Table 1: Variation in surface morphology of Y_2O_3 depending on preparation methods

Sr. No.	Preparation method	Grain Size		Morphology	Reference
		Length	Diameter(thickness)		
1	Solvothermal	~ 100 nm	10-30 nm	nanosheets	[9]
2	Precipitation	90 - 110 nm	30– 60 nm	monoclinic nanorods	[10]
3	Hydrothermal	20 – 40 nm	300 – 500 nm	nanorods	[11]
4	Facile hydrothermal	5-7 μm	2-3 μm	different flowers like	[13]
5	Hydrothermal (oxo-isopropoxide)	-----	110 -140 nm	spherical	[16]
6	Pechini sol-gel	-----	30 - 40 μm	spherical	[10,12]
7	Tartaric acid-assisted sol-gel	-----	20-40 nm	spherical	[25]

II. SURFACE MORPHOLOGY OF Y_2O_3

Yttrium oxide can be prepared by different methods and each preparation method can be used for particular characteristics. Different aspects of Y_2O_3 with rare earth and non-rare earth doped different shapes (wires, rods, cones, sphere and flower like) surface morphology and different crystal structures [9-17]. Transparent yttria ceramic was made by dry ball-milling method having grain size $6.67 \mu m$ and relative density was 99.8% [9]. Effect of preparation method on surface morphology and crystal size are summarized in following table. It is also found that by selecting appropriate organometallic precursor and controlling its combustion allow the synthesis of monoclinic as well as cubic Y_2O_3 nanorods [14]. Y_2O_3 changes morphology from nano sphere (30 - 50 nm) to flake and rod shape after mechanical alloying due to impact force, shear force and high energy during mechanical alloying process [15,16]. Luminescence properties of rare earth doped Y_2O_3 depends on the surface morphology of phosphor particle [18]. Y_2O_3 also exist in microprism like surface

structure [19]. Table (1) shows the variation in surface morphology of Y_2O_3 with preparation method.

III. EFFECT OF ANNEALING TIME

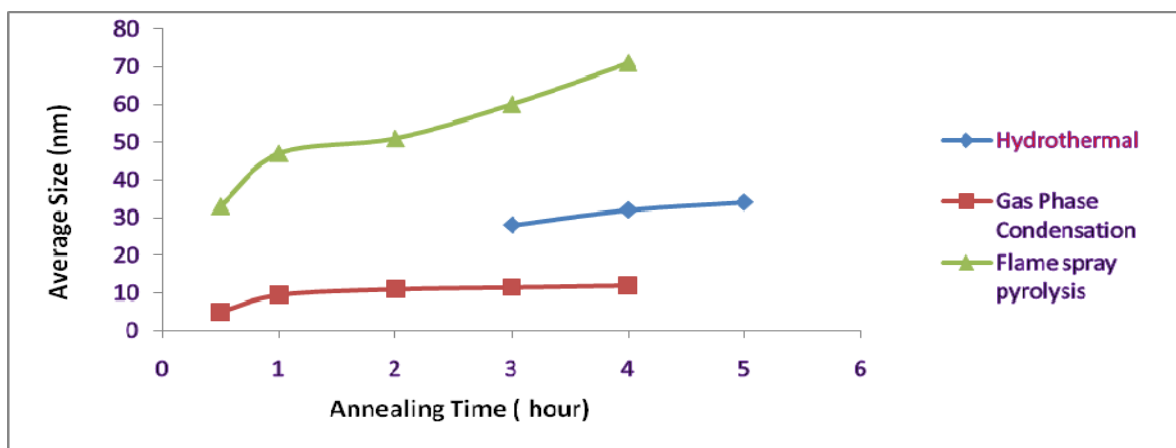
IV. A. On Size of Y_2O_3

From preparation method it is found that grain size and density of Y_2O_3 (yttrium oxide) depends on preparation method and sintering (annealing) time [10,18,20]. It was found that a high density and fine average grain size of Yttrium oxide can be simultaneously achieved when sintering temperature was $1600^\circ C$ (It is most suitable sintering temperature).

Size of Y_2O_3 (yttrium oxide) also depends on the annealing time taken during different preparation method [14,21,22]. Results on grain size depends on annealing temperature are summarized in following table (2). From the "Fig.1" it is found that when yttrium oxide prepared at different annealing time keeping annealing temperature constant, it is found that average particle size strongly depends on the annealing time. As increasing annealing time average particle size is found to be increases.

Table 2: Effect of annealing time on particle size of Y_2O_3

Sr. No.	Annealing Time (hour)	Average Particle size (nm) in different methods		
		Hydrothermal	Gas Phase Condensation	Flame spray pyrolysis
1	0.5	-----	5	33
2	1	-----	9.5	47
3	2	-----	11	51
4	3	28	-----	-----
5	4	32	11.5	71
6	5	34	-----	-----

**Figure 1: Variation of average particle size with annealing time.****B. On Photoluminescence Intensity**

“Fig.2” gives the excitation spectra of $Y_2O_3:Eu = 1$ mol% under 612 nm excitation prepared by precipitation method. “Fig.3” gives the effect of annealing time on emission spectra of $Y_2O_3:Eu = 1$ mol% prepared by precipitation method at 800 °C. From the emission spectra we observed that as we increase the annealing time the photoluminescence intensity is found to be increase, as observed by Gang Gu et al.[23]. A. Paulraj et al. and J.A. Nelson et al. finds that micro particle have better photoluminescence efficiency than nanoparticle under the same measurement condition [24]. A. Paulraj et al. explain this decrease in intensity as the nanoparticle scattered more light and second reason is that when particle size is reduced, the surface become more accessible to excitation centers, allowing for an increase in nonradiative surface recombination.

While, when Taxak et al. prepared nanocrystalline $Y_2O_3:Eu$ by Tartaric acid-assisted sol-gel method and reported that, photoluminescence efficiency of this nanophosphor is better than micro scale bulk material[25]. X. Zhang et al. prepare different shape yttrium oxide phosphor and conclude that, diffused reflectance is a very important factor which affect the photoluminescence efficiency[26]. From above discussion we see that annealing temperature affect the particle size. From Gang Gu et al.[23],result by Pulsed laser ablation (PLA) method and our precipitation (PPT) method result of $Y_2O_3:Eu$, we see that annealing temperature also affect the photoluminescence intensity, such results are summarized in following table(3).

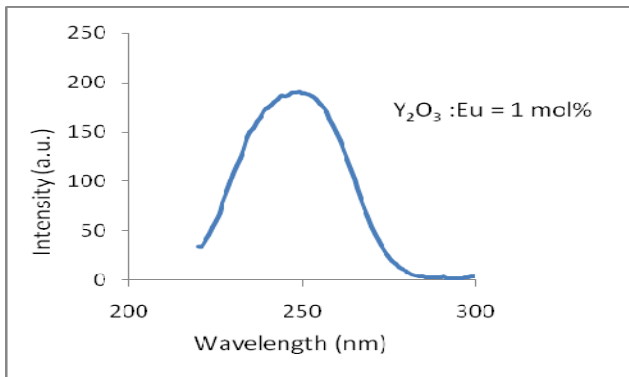


Figure 2: Excitation spectra of Y₂O₃:Eu = 1 mol% prepared by precipitation method

Figure 3: Emission spectra of Y₂O₃:Eu = 1 mol% at different annealing time prepared by precipitation method.

Table.3: Effect of annealing time on photoluminescence intensity.

Sr. No.	Annealing Time (hr)	Photoluminescence Intensity (a.u.)	
		Pulsed laser ablation method (PLA)[27]	Precipitation method (PPT)
1.	1	100	---
2.	2	250	89.03
3.	3	350	134
4.	4	400	138.5

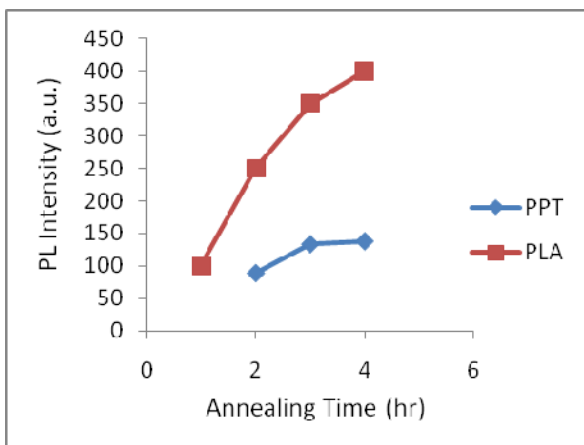


Figure 4: Variation of PL intensity with annealing time.

IV. APPLICATIONS

Ionic radius of Y³⁺ is approximately matched with rare earth ions, thus yttrium oxides with rare earth doping are used as engineering materials in many fields. Following are the importance applications of rare earth doped yttrium

A. Sensor

Due to high infrared transmission range (1-8 micron wavelength) together with high thermal stability and good resistance to erosion, makes yttrium oxide as an ideal for protection domes for infrared sensor, temperature sensor and for

solar cell. Also in ultrafast sensors that are used in γ -ray and x-rays. Rare earth doped upconversion phosphors are used for sensing purpose. Emission intensity depends on the input pump power density (power of exciting radiation) and increase in temperature. The internal heat produced from the samples are used in treatment of hyperthermia, cancer. Cubic phase Y₂O₃:Yb³⁺/Er³⁺/Eu³⁺ and Y₂O₃:Yb³⁺/Er³⁺ are found to be good IR sensor [28]. Consider the energy level diagram of Y₂O₃ samples having two excited state E-I and E-II and single ground state E_g as shown in "Fig.5". I₀ is the intensity of spectral line due to transition from E-I to E_g level and I₁ is the intensity of spectral line due to transition from E-II to E_g level, then we can write

$$\frac{I_1}{I_0} = \exp\left(-\frac{\Delta E}{kT}\right) \dots \dots \dots (1)$$

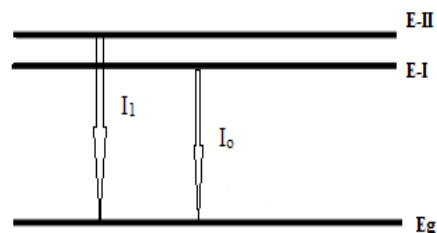


Figure 5: Energy level diagram of Y₂O₃

Where ΔE is energy difference between the E-I and E-II levels, k is Boltzmann's constant, T is absolute temperature and C is constant of proportionality, depends on sample. Eq. (1) is used for optical sensing purpose. By varying input power we can change the heat produced by sample and optical heat produced are used for different treatment purpose[28-30].

B. Photoluminescence

In the field of materials science yttrium oxide with rare earth doped find a number of applications such as imparting color to the television picture tubes. Also used in plasma and flat panel display. Yttrium oxide is a vital starting point in inorganic synthesis of compounds. The property of red light emission is used in making fluorescent lamps. Since, ionic radius of Y^{3+} is approximately matched with rare earth ions, thus yttrium oxides with rare earth doping ions are used in luminescence purpose. Rare earth Eu^{3+} and Tb^{3+} doped is a dominate red to orange range visible light emitting materials under mid UV and near UV excitation in commercial application on fluorescent lighting and display (PDP and FPD) due to its good luminescent characteristics, acceptable atmosphere stability, reduced degradation under applied voltage and lack of hazardous constituents [13, 31]. Current study shows that Y_2O_3 with rare earth ions doped can be use for solid state lighting purpose also[32]. Y_2O_3 with maximum 9.71 % rare earth are used in LEDs[33].

C. Cathodoluminescence

First demonstration of a high-spatial-resolution and multicolor imaging technique for observation of biological cells with using cathodoluminescence (CL) from nanophosphors have been observed. CL is emission from materials irradiated by accelerated electron beam. For CL imaging, $Y_2O_3:Tm$, $Y_2O_3:Tb$, $Y_2O_3:Eu$ were used as the phosphors[34]. The spectral bandwidth of the phosphors was narrow enough to distinguish the types of the phosphors. Yttrium oxide doped with europium ($Y_2O_3:Eu$) is a luminescent material with red-orange emission, excitation by electrons (cathodoluminescence)[35]. Cathodoluminescence can be used inside the transmission electron microscope to study phosphors such as $Y_2O_2S:Tb$, $Gd_2O_2S:Tb$ and

the quantum dots, which have wide ranging applications in scintillation phosphors through to the latest developments in high information content television displays under high energy radiation such as UV, X-rays, α -ray, β -rays femtosecond laser pulses and electron beams[36]. The current study shows that, the cathodoluminescent (CL) properties of $Y_2O_3:Eu$ thin films can be obtained by RF magnetron sputtering [37].

D. Fluorescence Bioimaging (FBI)

Rare-earth doped ceramics can be a good candidate, since these are known to emit efficient fluorescence in the NIR wavelength region by NIR excitation. Fluorescence bioimaging (FBI) is one of the key technologies for the biomedical sciences. It is used for the imaging of biological substances, and can also be utilized in techniques photo dynamic therapy, and drug delivery systems due to its potential of convenience, high resolution and high sensitivity [23,38]. Conventional boillable for imaging mainly include organic dyes (Fluorescent proteins) and quantum dots (QD) with few nano meter range. These boillable used for FBI under excitation of ultraviolet (UV) or short-wavelength visible light. In the case of fluorescent proteins, the probe proteins themselves and biological substances are damaged within a few minutes by the photo-toxicity due to the high quantum energy of the excitation light. Although light emitted from quantum dots can be utilized in various applications for periods of up to several tens of minutes, the potential toxicity associated with their use is a concern since quantum dots for the most part comprise toxic elements selected for their unique optical properties. For both of the probes, the strong scattering of the excitation light due to the short wavelength is a disadvantage for imaging with a deep observation depth. A solution to this problem involves a shift to a longer excitation wavelength. Rare-earth doped ceramic materials show efficient fluorescence under near infrared (NIR) excitation [39]. Current investigation shows that $Y_2O_3:Er$ particles and the surface modification of these particles with double layers of PAAc (acrylic acid) as an interfacing agent and acetal-PEG-*b*-PAMA led to successful NIR imaging nanoparticles[38,40]. Grain size of these particles is found to be 10

nm to 200 nm which are found to good for near infrared excitation.

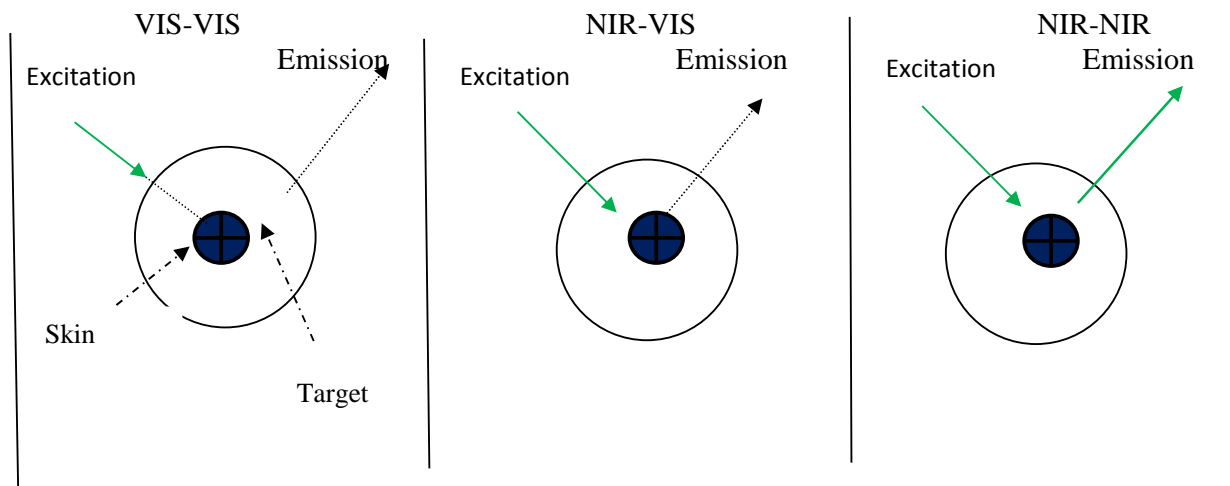


Figure 6: Advantage of NIR-NIR imaging system. Near infrared(NIR) emission by NIR excitation is observed using a NIR-NIR system. Due to weaker scattering and absorption, NIR light can penetrate deeper into/from tissues. In contrast, excitation light in the visible (VIS) region cannot reach the imaging target in tissues in the conventional VIS-VIS imaging. In upconversion (NIR-VIS) imaging, although NIR excitation light can reach its target in tissues, only a weak VIS emission can be obtained [41].

Also the Plasmon-enhanced upconversion luminescence was observed in Au/SiO₂/ Y₂O₃: Yb³⁺, Er³⁺. The use of near infrared (NIR) light for biomedical photonics in the wavelength region between 800 and 2000 nm, called as “biological window”, has received particular attention since water and biological tissues have minimal optical loss due to scattering and absorption as well as auto fluorescence in this region. Y₂O₃:Yb,Er which show strong NIR emission under NIR excitation (NIR-NIR emission). We also demonstrate that NIR emission can be observed through swine colon wall [41]. “Fig.6”, shows the advantage of NIR-NIR imaging System.

E. Additives Coatings

Y₂O₃ also used as additives in the coatings used in high-temperature applications, paints and plastics for guarding against UV degradation. Due to its high capacity of resisting a high transverse electric field, good current density breakdown field (J-E) characteristics, lowest effective oxide charge interference trap density [8,9] and large conduction band offset [42], yttrium oxide used as a functional GaN-based MOS device.

F. Ceramic Laser

Polycrystalline ceramic are new types laser host materials, due to wide band gap, large nonlinear refractive index, high power output (good efficiency), low scattering loss and large melting point [43-47], Eye safe laser source are have variety of applications such as in medical for stone retropulsion and ablation of hard tissue, for remote sensing of atmospheric CO₂ and H₂O using LIDAR techniques as well as frequency conversion by optical parametric oscillator [44,45]. High power lasers are widely used in a variety of applications, including materials processing, remote sensing, free-space communications, laser particle acceleration, gravitational wave interferometers, and even inertial confinement fusion (ICF) [49]. Nd:Y₂O₃ and Yb:Y₂O₃ ceramics laser materials as having an extra advantage over single crystals. It is very hard to grow a single Y₂O₃ crystal because its melting temperature is 2430 °C. The sintering temperature for Y₂O₃ is some 700 °C lower than its melting point, so that large Y₂O₃ ceramics could be manufactured using a vacuum sintering method [48,49]. Nd:Y₂O₃ (nano), Nd:Y₂O₃ (ceramic) shows radiative life time of 4.49 ms, 4.79 ms respectively and corresponding quantum efficiency is 44.32 %

and 21.71 % [50]. In addition to this Tm doped Y_2O_3 can be used as eye safety laser [46]. Y_2O_3 use to make YAG which good laser host [49-51].

Some of the other applications include additives in steel, non-ferrous alloys and iron,

making permanent magnets [52]. Yttrium iron garnets which are derived from yttrium oxide are used as powerful microwave filters [50-52]. Laser characteristics of some rare earth doped yttrium oxide are as shown in table (4).

Table 4: Laser characteristics of rare earth doped Y_2O_3 .

Sr. No.	Sample	Pump power	Power out put	Optical efficiency	FWHM (nm)	Emission (nm)	Life time	Reference
1	$Y_2O_3:Yb^{3+}$	15.5 W	2.7 W	17 %	1.6	1078	1.1 ps	[43]
2	$Y_2O_3:Yb^{3+}$	4 W	1.5 W	32 %	1.6	1037	430 fs	[44]
3	$Y_2O_3:Ho^{3+}$	9 W	2.5 W	27.9	0.15	2118.8	11.3 ms	[45]
4	$Y_2O_3:Yb/Er^{3+}/Tm^{3+}$	60 mW	1.67 mW	2.79 %	----	White light	---	[46]
5	$Y_2O_3:Nd^{3+}$	742 mW	160 mW	32 %	---	1074.6 , 1078.6	-----	[51]

V. CONCLUSION

Recent technology facing problems of efficient and environment friendly materials, thus Y_2O_3 can be a promising candidate in luminescent display devices. Non-toxicity, bio comparability and abundance in nature make them excellent host for light emitting materials in laser, sensor devices and as phosphor for green light energy source (LEDs). Since we can use yttrium oxide in current immersing field such as in fluorescence bioimaging, which can also be utilized in techniques photo dynamic therapy and drug delivery systems due to its potential of convenience, high resolution and high sensitivity. In addition to these Y_2O_3 can be used as additive coating in optoelectronic devices, additives in steel, non-ferrous alloys and iron, making permanent magnets and microwave filters. Y_2O_3 of different morphology and of various size particles can be formed easily which increases its smartness nature. Since size of the luminescence material is very important in high resolution display materials.

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