Luminescence Study of Red Light Emitting Y$_2$O$_3$:Sm$^{3+}$ Nanophosphors and Enhancement by Co-doping with Gadolinium oxide

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Abstract: This work presents the optical and structural properties of samarium oxide doped and gadolinium oxide co-doped yttrium oxide nanophosphors prepared by Combustion method. The photoluminescence emission intensity was maximum for 2wt% Sm$^{3+}$ doped Y$_2$O$_3$ powders, that results in$^6$G$_{5/2}$ -$^4$H$_{5/2}$ transition within Samarium, emits red light at 608 nm under the excitation of 260 nm. In the case of co-dopant, maximum intensity is obtained for 3wt% Gd$^{3+}$ under the excitation of 255 nm. The Y:Sm:Gd exhibit luminescence intensity of 4.21 times more than that of Y:Sm nanophosphors. These results indicate that the prepared nanophosphors can be used in optoelectronic devices.

Keywords: Bandgap, Co-doping, Energy transfer, Nanophosphor.

I. INTRODUCTION

The replacement of traditional lighting system by the technology of luminescence lighting has greatly influenced the life style of present modern people. The luminescence devices plays an important role in the life of modern civilization that it is impossible for the people to imagine a life without these [1]. For the last ten years, one of the important sources of lighting is white LEDs. This generation of white LEDs and coloured light has considered to be the market driver in the modern age. Materials that can emit light, especially in the visible range are known as ‘luminescent materials’ or phosphors. Generally, phosphors consist of host element and intentionally added small amount of impurity known as activator. Phosphors can be oxides, alkali and alkaline earth halides, phosphates, sulphates etc. The excitation energy is absorbed by the phosphor matrix. Thus the chemistry between crystalline structure and the matrix composition plays an important role. Thus we selected yttrium oxide (Y$_2$O$_3$) as our host metal. Y$_2$O$_3$ is capable of making non-radiative relaxation of the excited states because it possesses low phonon energy. Moreover, Y$_2$O$_3$ is capable of absorbing infrared radiation and emit visible light. Yttrium oxide alone does not show any luminescence. It will emit light after doping with some metals known as activators in small amount. In order to get red or intense reddish orange emissions, host lattice are doped with certain rare-earth ions [2]. A detailed study has been carried out for Eu$^{3+}$ doped Y$_2$O$_3$ [3],[4]. But a little study has been done in the case of energy transfer and luminescence characteristics of samarium oxide (Sm$^{3+}$) doped Y$_2$O$_3$ nanophosphors [5]. In some cases, the activator cannot directly absorb the excited radiation. In the case of such luminescent materials, the situation is much more complicated. So, we add one more ion into the host matrix. This additionally added ion can absorb the radiation that is excited and shift it to the activator. In such cases, the ion that absorbs the exciting radiation is called sensitizer. But the sensitizer does not have much influence on emission spectrum as compared to activator. Normally, sensitzers act as donors and activators act as acceptors. During excitation of the sensitizer, transfer of energy takes place between the sensitizer and lanthanide ion. With the help of activators, and various sensitzers we can synthesize different phosphors that emit particular colour and enhance their luminescence. That is why we focus our attention in our work mainly on the development of red phosphors.

II. EXPERIMENTAL

For synthesis work, yttrium oxide (Y$_2$O$_3$), samarium oxide (Sm$_2$O$_3$), nitric acid (HNO$_3$) and citric acid (C$_6$H$_8$O$_7$) were used as the precursor materials. The procedure is schematically shown in Fig. 1a.

In the second step gadolinium oxide has been added as co-dopant into Y$_2$O$_3$:Sm nanophosphors and carried out detailed study concerned with the effects of co-doping.

The structure and crystallinity of the powders were analysed by X-ray diffraction (XRD) using Rigaku Miniflex 600 (λ = 0.15406 nm, 40 kV, 15 mA). The spectra of FTIR were studied in the wavelength range of 400-4000 cm$^{-1}$ using Agilent Technologies-Cary 630 with ATR. With the help of UV-Vis spectrophotometer, Perkin Elmer Lamda, in the wavelength range 200-800 nm, the diffuse reflectance spectra (DRS) were investigated. The studies regarding photoluminescence (PL) were characterized on Agilent Technologies-Cary Eclipse Fluorescence Spectrometer. The studies related to the size and morphology of powders were carried out by JeolJEM 2100 high resolution transmission electron microscopy (TEM). The machine was operating at an accelerating voltage of 200 kV.
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![Diagram of the preparation process](image)

**Fig.1a: Schematic diagram for the preparation of Sm³⁺ doped Y₂O₃ nanophosphors**

### III. RESULTS AND DISCUSSIONS

#### A. Structural Analysis - XRD

In this work, we mainly concentrated on the optimization of the optical characteristics of nanophosphors in relation to samarium concentration. The results show that the PL intensity of 2wt% Sm³⁺ doped Y₂O₃ powders were seem to be maximum when compared to other Sm³⁺ concentrations. Fig. 2a shows the XRD pattern of the phase formation of undoped and 2wt% Sm³⁺ doped Y₂O₃ compounds. From the XRD pattern we confirm that the as formed compound is of single phase. The supporting evidence was obtained from the diffraction peaks which was sharp and single [6]. The crystal structure of the phosphor was not influenced by the introduction of Sm³⁺ ions [7]. Substitution of Y³⁺ with Sm³⁺ ions are possible because Y³⁺ has the ionic radii of about 0.93 Å which are very close to ionic radii of Sm³⁺(0.96 Å). Thus we confirm that samarium ions were properly substituted in yttrium sites because no peaks correspond to samarium or its compounds seem to be present in the XRD pattern. The Rietveld refinement of 2wt% Sm³⁺ doped Y₂O₃ sample is shown in Fig.2b. This also reveals that the chemical composition of the compound synthesized by this method are pure[8]. The (hkl) values of the peaks are depicted in the XRD pattern. The crystal structure was cubic with space group Ia3 which was confirmed by JCPDS Card No.00-025-1200 [9]. The most intense peak was observed at 2θ = 29.1°. This corresponds to the plane (222)[6]. Fig.2c shows the XRD spectrum for 2wt% Sm³⁺ doped Y₂O₃ phosphors in as synthesized condition and annealed at various temperatures. The XRD patterns of the powders in as prepared condition showed broad and very weak peak. This indicates that the precursor has decomposed into Y₂O₃ but it is not well crystalline[8]. The appearance of broad peaks indicates the formation of nano sized particles. Xu et al., found no peaks corresponding to cubic phase of Y₂O₃ when the temperature was at 573 K. Moreover, it was noticed that after annealed at 723 K, the compound remains in amorphous state. When the temperature was increased to 873 K, they observed diffraction peaks. According to Gowd et al., broad and weak diffraction peaks were obtained when the sample was annealed at 773 K. We also obtained weak and broad peak at 773 K. This occurrence of crystallization in different temperatures is due to the difference in the method chosen and also the precursor materials [10]. Moreover, when the calcined temperature increases, the diffraction peaks become sharper and stronger. This shows an enhancement in the crystallite size and crystallinity with increase in temperature [8]. This transformation with temperature increment may be due to enhanced oxidation kinetics[11]. Attainment of good crystallinity in the case of nanoparticles can be confirmed by the presence of high intensity of the peaks[12]. We observed that when the temperature is increased, the peaks become more sharper along with increase in intensity. The studies thus confirmed the phenomenon of crystallinity improvement with temperature increment[13]. The FWHM of the peak is found to be more in the case of 773 K annealed sample as compared to the 1173 K. It was expected that with the increase in temperature, width should get narrower. This is quite clear that this is because of the increase in crystallinity of the Y₂O₃:Sm³⁺ nanopowders [14]. During heat treatment, as synthesized nanoparticles appear to form the aggregates. This results in large crystallite size of the particles and reduction of lattice constant [15]. The increment in crystallite size and the reduction of lattice parameter with the increment in temperature indicates that the lattice planes are so close. This leads to a decrease of the dislocation density and an increase of the density [10]. We observed the appearance of tensile strain. Because there appears peak shifting towards longer angles with increase in temperature. Crystallinity plays a very significant role in the case of nanophosphors because attaining crystallinity indicates stronger luminescence and lesser traps [16]. In order to calculate the value of grain size(D) at various temperatures and concentrations, the high intensity peak (222) was used [15]. Using Debye’s Scherrer’s formula, crystallite size has been calculated.

![XRD Spectra](image)

**Fig.2a: XRD Spectra of un-doped and 2wt% Sm³⁺ doped samples**

Grain size grow with temperature. For nanophosphors, grain size growth results in the reduction of surface area of the particles. This results in luminescence enhancement.
This was because of the reduction of surface defects and the non-radiative rates [17]. Quite interestingly, we noticed that the average crystallite size remain in nanometer regime after annealing at high temperature [13].

Fig.2b: Rietveld Refinement of 2wt% Sm$^{3+}$ doped Y$_2$O$_3$ sample

![Rietveld Refinement of 2wt% Sm$^{3+}$ doped Y$_2$O$_3$ sample](image)

Fig.2c: 2wt% Sm$^{3+}$ doped samples annealed at different temperature

![2wt% Sm$^{3+}$ doped samples annealed at different temperature](image)

Fig.2d: Samples of various Sm$^{3+}$ concentration annealed at 1173 K.

![Samples of various Sm$^{3+}$ concentration annealed at 1173 K.](image)

Fig.2e: Hall Williamson plot to calculate the crystallite size

![Hall Williamson plot to calculate the crystallite size](image)

Optimised dopant concentration is obtained after adding 2wt% of Sm$^{3+}$ into Y$_2$O$_3$. To this we add different percentage of gadolinium oxide (Gd$_2$O$_3$) as co-dopant. We obtained the optimized concentration when Sm$^{3+}$ is at 2wt% and Gd$^{3+}$ is at 3wt%. The peaks that we obtained after the addition of Gd$^{3+}$ (Y$_2$O$_3$:Sm$^{3+}$:Gd$^{3+}$) corresponds to Y$_2$O$_3$ cubic structure confirmed by JCPDS file as depicted in Fig.3a and Fig.3b. A slight peak shift appears as a function of annealing temperature. The peak appears at $2\theta = 29.16^\circ$, $29.17^\circ$, $29.20^\circ$, $29.21^\circ$, $29.22^\circ$ for the powders calcined at 773 K, 873 K, 973 K, 1073 K and 1173 K respectively. This results indicates that homogeneous powder of Y$_2$O$_3$:Sm$^{3+}$:Gd$^{3+}$ has been obtained at higher temperature where re-distribution of Y$^{3+}$, Gd$^{3+}$ and Sm$^{3+}$ which have different size through inter diffusion. The cationic re-distribution takes place because of the concentration gradients within the precursor. Lattice parameter confirms the formation of homogeneous oxides. The lattice parameter increases with increase of co-dopant. The Sm$^{3+}$ have ionic radius which is larger than Gd$^{3+}$. Therefore, Sm$^{3+}$ is more effective in enlargement of cell parameter than Gd$^{3+}$ [19]. Co-doping does not result in phase change, maintained the crystal structure and lattice strain has been noticed. The presence of this lattice strain was due to change in the lattice energy. Calculations of structural parameters after co-doping are given in Table-II.

![Hall Williamson plot to calculate the crystallite size](image)
Table-I: Structural parameters of Y$_2$O$_3$ phosphors

| Temperature (K) | FWHM (degree) | Lattice Parameter | Crystallite Size (nm) | Interplanar Spacing (nm) | Strain (10$^{-3}$) | Particle Density | Dislocation Density |
|-----------------|----------------|-------------------|-----------------------|--------------------------|---------------------|------------------|---------------------|
| 773             | 0.993          | 10.614            | 8.25                  | 5.41                     | 3.06                | 0.04             | 5.017               | 3.97                |
| 873             | 0.824          | 10.599            | 9.94                  | 6.54                     | 3.059               | -0.03            | 5.037               | 3.94                |
| 973             | 0.630          | 10.584            | 13.01                 | 9.09                     | 3.055               | -0.02            | 5.059               | 3.90                |
| 1073            | 0.443          | 10.579            | 18.52                 | 12.1                     | 3.054               | -0.02            | 5.066               | 3.89                |
| 1173            | 0.272          | 10.564            | 30.08                 | 19.7                     | 3.049               | -0.01            | 5.088               | 3.86                |

Concentration (%) of samples annealed at 1173 K

|           | 1%      | 2%      | 3%      |
|-----------|---------|---------|---------|
|          | 0.361   | 0.272   | 0.359   |
|          | 10.560  | 10.564  | 10.593  |
|          | 22.71   | 30.08   | 22.84   |
|          | 14.9    | 19.7    | 15.0    |
|          | 3.048   | 3.049   | 3.058   |
|          | -0.01   | -0.01   | -0.01   |
|          | 5.093   | 5.088   | 5.046   |

Table-II: Structural parameters of Gd$^{3+}$ co-doped Y$_2$O$_3$ phosphors

| Temperature (K) | FWHM (degree) | Lattice Parameter | Crystallite Size (nm) | Interplanar Spacing (nm) | Strain (10$^{-3}$) | Particle Density | Dislocation Density |
|-----------------|----------------|-------------------|-----------------------|--------------------------|---------------------|------------------|---------------------|
| 773             | 0.926          | 10.599            | 8.85                  | 5.81                     | 3.059               | -0.04            | 5.037               | 3.94                |
| 873             | 0.729          | 10.596            | 11.25                 | 7.38                     | 3.058               | -0.03            | 5.042               | 3.93                |
| 973             | 0.551          | 10.585            | 14.87                 | 9.77                     | 3.055               | -0.02            | 5.057               | 3.90                |
| 1073            | 0.429          | 10.582            | 19.10                 | 12.5                     | 3.054               | -0.01            | 5.062               | 3.90                |
| 1173            | 0.248          | 10.578            | 33.05                 | 21.9                     | 3.053               | -0.01            | 5.067               | 3.89                |

Concentration (%) of samples annealed at 1173 K

|           | 1%      | 2%      | 3%      | 4%      |
|-----------|---------|---------|---------|---------|
|          | 0.351   | 0.340   | 0.248   | 0.351   |
|          | 10.574  | 10.575  | 10.578  | 10.582  |
|          | 23.35   | 24.11   | 33.05   | 23.33   |
|          | 15.3    | 15.8    | 21.9    | 15.3    |
|          | 3.052   | 3.052   | 3.053   | 3.055   |
|          | -0.01   | -0.01   | -0.01   | -0.01   |
|          | 5.074   | 5.073   | 5.067   | 5.061   |
|          | 3.88    | 3.88    | 3.89    | 3.90    |

Fig.3a: XRD Spectra of 3wt% Gd$^{3+}$ samples annealed at various temperatures.

Fig.3b: XRD Spectra of various Gd$^{3+}$ concentration annealed at 1173 K.

### FTIR

Fig.4a and 4b depicts the Fourier transform infrared spectra of un-doped yttrium compound, as prepared and annealed (Y$_2$O$_3$-2wt%Sm$^{3+}$) doped samples and co-doped with 3wt% Gd$^{3+}$ samples annealed at different temperatures in the range 400-4000 cm$^{-1}$ [20],[21]. A characteristic band was observed at 3430 cm$^{-1}$ in the case of samples annealed at 773 K. This band was due to the hygroscopic nature of rare earth, O-H stretching deformation vibrations of H$_2$O. For pure yttrium phosphor, this absorption band is almost absent. In the case of luminescent materials, the presence of –OH group results in the quenching process of emission which in turn reduces the luminescence efficiency [22]. Heat treatment is the only remedy to overcome this [23]. The bands with low intensity can be seen in the region from 1200-1700 cm$^{-1}$. This was assigned to the presence of carbonate species which was formed by the action of CO$_2$ molecules onto Y$_2$O$_3$ surface. Mokkelbost et al., suggested that the prepared sample shows the presence of few amount of carbonate species after annealing at higher temperature around 1273 K for half a day. The peaks associated with the CO$_3^{2-}$ and presence of adsorbed water in the case of as-prepared samples reduces when the samples annealed to 973 and 1173 K [24]. The decrease of carbonate group with increase in temperature shows the reduction of carbon content in annealed samples [6]. Additional bands present in 1120 cm$^{-1}$ was ascribed to the asymmetric vibrations of COO$^-$ that arises from citric acid [22].
The characteristic peak located at 609 and 561 cm\(^{-1}\) are attributed to the Y-O stretching vibrations of cubic Y\(_2\)O\(_3\) [20]. As the temperature increases, the peaks become strong. Upon heat treatment, organic composition completely vanishes and at the same time, Y\(_2\)O\(_3\) band becomes much stronger, showing the perfect crystallization of doped and co-doped samples [13]. The FTIR results do not show the presence of any organic residues that quenches the emission [25]. The features discussed above indicates a better stoichiometry and crystallization of Y\(_2\)O\(_3\) powders, which was confirmed by XRD observations [22].

In order to obtain the basic solid state physics, the band gap determination is very important. Table-III shows the band gap of un-doped, doped (2wt% Sm\(^{3+}\)) and co-doped (3wt% Gd\(^{3+}\)) yttrium oxide powder phosphors. In the case of nanophosphors, energy gap plays an important role. It determines their applications in optoelectronics. The commonly used method to determine the band gap is the Tauc Plot. The optical band gap energy is calculated for direct allowed transition. Because it is good for linear fitting in the band edge region [20]. Using diffuse reflectance spectrum, band gap can be calculated by Kubelka-Munk Theory [6].

From the table it is clear that \(E_g\) values are more for calcined samples as compared to as –prepared samples. The obtained \(E_g\) values are in good agreement with the literature. \(E_g\) values vary from 5.56-5.74 eV for doped samples and 5.37 to 5.42 eV for co-doped samples. The lattice has certain degrees of structural order-disorder. Within the optical band gap, there will be a number of intermediate energy level. This too have direct influence on each other. This may be the reason for the variation in the band gap [24].

C. Optical Properties - Diffuse Reflectance

Fig.5a-5d shows the DRS spectra of un-doped, doped (2wt%Sm\(^{3+}\)) and co-doped (3wt%Gd\(^{3+}\)) Y\(_2\)O\(_3\) powder phosphors as a function of various concentration and annealing temperatures recorded in the wavelength range 200-700 nm [20]. CdSO\(_4\) sample is taken as reference in these cases [6]. A sharp band was observed at 210 nm in the case of un-doped yttrium samples. This indicates that light which has 210 nm wavelength was absorbed [6]. In the case of doped Y\(_2\)O\(_3\) samples, absorption band was observed at 230 nm and for co-doped sample, absorption band was at 217 nm. There occurs difference in the position of the peak in the case of as –prepared and samples annealed at high temperature. In the case of doped samples, the absorption edge is deviated towards longer wavelength (red) region when compared to un-doped samples. This is because of the variation in the crystallite size [6].
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![Graph 1](image1.png)

**Fig.5c:** DR Spectra of co-doped samples as a function of concentration

![Graph 2](image2.png)

**Fig.5d:** DR Spectra of co-doped samples as a function of temperature

### Table III Variation of bandgap with temperature

| No. | Sample Name       | Temperature (K) | Band gap (eV) |
|-----|-------------------|-----------------|---------------|
| 1.  | Pure Yttrium oxide | 1173 K          | 5.6 eV        |
| 2.  | Y$_2$O$_3$:Sm     | 973 K           | 5.56 eV       |
| 3.  | Y$_2$O$_3$:Sm     | 1073 K          | 5.65 eV       |
| 4.  | Y$_2$O$_3$:Sm     | 1173 K          | 5.74 eV       |
| 5.  | Y$_2$O$_3$:Sm:Gd  | 973 K           | 5.37 eV       |
| 6.  | Y$_2$O$_3$:Sm:Gd  | 1073 K          | 5.40 eV       |
| 7.  | Y$_2$O$_3$:Sm:Gd  | 1173 K          | 5.42 eV       |

D. TEM

Field Emission Transmission Electron Microscopy (FE-TEM) and Selected Area Electron Diffraction (SAED) of the prepared samples annealed at 773 K and 1173 K has been carried out to study the crystal quality and to obtain much more detailed information regarding atomic structure as shown in Fig. 6a-6h [26]. For the synthesis of samarium doped yttrium oxide nanophosphors and co-doped samples, the role of reaction temperature on the size and morphology were noticed [27]. FE-TEM image of the samples prepared at 773 K confirmed that the particles are aggregated [9]. And moreover, the shape of the samples are not identified properly. For samples annealed at 1173 K, each particle contain a large number of nanocrystals. We noticed from TEM that Y$_2$O$_3$:Sm$^{3+}$ and Y$_2$O$_3$:Sm$^{3+}$:Gd$^{3+}$ nanophosphors are spherical in shape [15]. Thus a structural evolution occur from amorphous to crystalline state [28]. There is an increment in the particle size with increase in annealing temperature which was proved from XRD data. Thus, obviously, the particle exhibit stronger luminescence. When the temperature increases, particle size increases, surface to volume ratio decreases, scattering of light reduces which in turn increases the efficiency. Thus we can say that one of the factors that depend on increase of particle size is sintering or hard agglomeration [16]. Very keen observation of the images shows damage free and clear lattice fringes. The interspacing is 0.306 nm that corresponds to (222) plane. It is quite natural that when the size of particle is smaller, surface area of nanoparticle is larger which in turn results in large number of defects. On account of this, there occurs a reduction in the luminescence intensity. In our Y$_2$O$_3$ nanophosphor, the lattice fringes shows that the quality of the crystal is very high with small distortions[26]. Thus we obtain strong luminescence intensity in our sample. Because the electrons and holes that resides in the excited state comes to ground state through optically radiative recombination routes [26]. The size of the particle that we obtained from TEM (25-30nm) is slightly larger than what we obtained from XRD. This is because line width of XRD depends mainly on the coherent domains. But that requirement is absent in the case of TEM and it measures the actual particle size [29].The SAED pattern of the 1173 K annealed sample is depicted in Fig.6a and 6b.
Fig. 6b: FETEM of $\text{Y}_2\text{O}_3$:Sm$^{3+}$ nanophosphor annealed at 1173 K

Fig. 6c: FETEM of $\text{Y}_2\text{O}_3$:Sm$^{3+}$ nanophosphor - image of lattice fringes at 773 K

Fig. 6d: FETEM of $\text{Y}_2\text{O}_3$:Sm$^{3+}$ nanophosphor - image of lattice fringes at 1173 K

Fig. 6e: FETEM of $\text{Y}_2\text{O}_3$:Sm$^{3+}$ nanophosphor- SAED at 1173 K

Fig. 6f: FETEM of $\text{Y}_2\text{O}_3$:Sm$^{3+}$:Gd$^{3+}$ nanophosphor annealed at 1173 K

Fig. 6g: FETEM of $\text{Y}_2\text{O}_3$:Sm$^{3+}$:Gd$^{3+}$ nanophosphor - image of lattice fringes at 1173 K
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Modification of luminescence spectrum occurs when Sm³⁺ ions are incorporated into Y₂O₃ crystal. In the case of Sm³⁺, transitions occur from excited ⁴G⁵/², level to ⁴Hj (j=5/2,7/2,9/2……) levels of ⁴f configuration. The most intense peak centred at 608 nm is owing to hypersensitive electric dipole transition ⁴G⁵/²-⁴H⁷/². Absence of inversion symmetry in Sm³⁺ site is responsible for this transition.

In order to get the optimum dopant concentration, a series of dopant concentration of 1%, 2%, 3%, 4% and 5% in Sm³⁺ wt% were studied. Fig 8a shows the dependence of dopant concentration on PL of Sm³⁺ doped Y₂O₃ nanocrystals. By changing the concentration amount of Sm³⁺, spectral position remain unchanged but PL intensity changes. As depicted in figure, initially the luminescence intensity increase with increase in concentration of Sm³⁺; then it starts decreasing when the Sm³⁺ concentration exceeds 2wt%. There occurs considerable variation in the luminescence intensity in the Sm³⁺ range of 1-3wt% and maximum intensity was obtained at 2wt% of Sm³⁺ concentration [29]. This indicates the occurrence of a strong quenching process at concentrations larger than 2wt% of Sm³⁺ [30].

One of the reasons for quenching process may be leaching out of Sm³⁺ when the dopant is at higher concentration. For verification, we have observed the value of lattice parameter of all doped samples. The result shows that lattice constant increases with increasing Sm³⁺ doping concentration. This trend can be assigned to the fact that ionic radius of Sm³⁺ is slightly larger than ionic radius of Y³⁺ ions. This results indicates the perfect incorporation of Sm³⁺ into Y₂O₃ lattice upto 2wt% of Sm³⁺ ion and no leaching out of dopant has appeared. This unusual attitude of luminescence property must be due to some other reason [13]. It has been found that excessive doping of Sm³⁺ ion reduces the luminescence intensity[31]. The quenching occurs at a particular concentration, where the average distance between luminescent centres, that emit light decreases [32]. An output limiting effect occurs during the interaction between Sm³⁺ ions when its concentration is too high. Detailed studies indicated that quenching occurs beyond optimal concentration of dopant is because of energy transfer among adjacent luminescent centres via cross-relaxation [27].

In our case, the luminescence concentration quenching occurs when Sm³⁺ was increases beyond 2wt%. When the Sm³⁺ concentration is less than 2wt%, nearby ions of Sm³⁺ are isolated and only very few defects will transfer its energy to the nearby traps. Thus, the quenching of luminescence is not predominant. When the concentration of dopant increases to 2wt%, the Sm³⁺ ions becomes more closer so that they can transfer excitation energy among each other resonantly. When the concentration of luminescent centre exceeds 2wt%, the distance between nearby Sm³⁺ ions are less. Thus Sm³⁺ ions lose the energy that are excited non-radiatively. This supports the quenching effect and ultimately luminescence intensity decreases. By make use of wavelength in the absorption band, the luminescent centre is excited. After a short while this will come down to ⁴G⁵/² level non-radiatively then relax to the ground state radiatively by the photon emission that corresponds to Sm³⁺ transitions [32].
Influence of Annealing Temperature on Photoluminescence

The photoluminescence emission spectra of Y$_2$O$_3$:Sm$^{3+}$ phosphors calcined at different temperatures 773 K to 1173 K is shown in Fig.7c. The optimum concentration of 2wt% of Sm$^{3+}$ were taken. This study presents luminescence dependence on temperature. So it is very important to connect the luminescence character with the changes takes place in the microstructure because of thermal processing and gain insight on the luminescence yield of the material. The luminescence results indicate that the emission intensity of the as-synthesized sample is very weak. We noticed an increment of emission intensity with increase in temperature [24]. When the sample annealed at 973 K, the intensity increases drastically. This is on account of good dispersion of dopant into the host and increased crystallinity growth [6]. This obtained result can be explained in detail as the high processing temperature supplies high energy and thus there occurs an improvement in the crystallinity and crystal growth. The enhancement in the case of emission of red colour can be done with increasing the number of oxygen vacancies. Tingting Yan et al., reported the high luminescence performance of carbon doped Eu$_2$O$_3$ because of more oxygen vacancies. Gu et al., also reported the same result in the case of SnO$_2$:Ce$^{3+}$. It must be noted that the oxygen vacancies generally behave as radiative centres in the case of luminescence. We noticed an increase in intensity of emission peak with increase in annealing temperature. Quite interestingly, when we compare the intensity of as-prepared sample and samples annealed at 973 K, increment of 1.09 orders of magnitude can be observed. This is because the formed cubic yttria phase is well crystalline as indicated in XRD spectra [13].

Moreover, our sample does not show the presence of monoclinic phase. If the sample is monoclinic, the strongest emission $^5G_{7/2}$ to $^7H_{5/2}$ will be at a wavelength of 623 nm. Thus we confirm that the obtained samarium doped yttria by the combustion method is of single phase cubic [29].

However, there is a direct relation between morphology of Y$_2$O$_3$:Sm$^{3+}$ nanostructure and emission intensity. It is well-known fact that spherical sample exhibit good luminescence properties. This is because the packing density is more for spherical shaped sample as compared to other shapes. Moreover, this spherical shaped sample decreases the scattering of light and non-radiation. The Y$_2$O$_3$:Sm$^{3+}$ nanospheres that we obtained have spherical shape, with no agglomeration and narrow distribution of particle size. Thus this can be applied in various fields such as phosphors, laser materials, field emitter and in optoelectronic devices [8].

Influence of Co-doping on Photoluminescence

Addition of Gd$_2$O$_3$ into the Y$_2$O$_3$:Sm system results in the luminescent enhancement of the resultant particles. By keeping the value of Sm$^{3+}$ as constant (2wt%), we added different concentrations of Gd$^{3+}$ and finally obtained 3wt% Gd$^{3+}$ as the optimised co-doped value. Fig. 8a shows the comparison of luminescence spectra of two samples. The incorporation of Gd$^{3+}$, doesn’t make any change in the peak position of the $^5G_{7/2}$ to $^7H_{5/2}$ transition. But the intensity enhances which indicates that the emission of red light is successfully sensitized by Gd$^{3+}$ ions by energy transfer from Gd$^{3+}$ to Sm$^{3+}$. When the Gd$^{3+}$ addition increases, intensity of the 608 nm emission also increases. Covalency increment occurs when Gd$^{3+}$ is added. If we consider the bond structure of Sm$^{3+}$ - O$^{2-}$-Y$^{3+}$/Gd$^{3+}$, the electronegativity of Y$^{3+}$ is 1.22 and that of Gd$^{3+}$ is 1.20. The attraction between electrons and ions occurs in the form Y$^{3+}$ > Gd$^{3+}$. Thus the energy required to transfer the electrons from O$^{2-}$ to Sm$^{3+}$ increase in the same way. Charge transfer becomes easier if we replace Y$^{3+}$ with Gd$^{3+}$ that results in enhancement of intensity. The intensity of Gd$^{3+}$ co-doped Y$_2$O$_3$:Sm sample is 4.21 times that of Y$_2$O$_3$:Sm sample.
Luminescence Study of Red Light Emitting Y$_2$O$_3$:Sm$^{3+}$ Nanophosphors and Enhancement by Co-doping with Gadolinium oxide

**IV. CONCLUSION**

2wt% Sm$^{3+}$ doped Y$_2$O$_3$ nanophosphors and co-doped with 3wt%Gd$^{3+}$ has been prepared by combustion method. XRD studies confirms that the obtained product has cubic phase. Furthermore, no extra peaks has been observed. The size of the particle increases with temperature. The size calculated by the Debye-Scherer formula and Williamson-Hall plot are in accordance with each other. Band gap varies from 5.56 – 5.74 eV for Y$_2$O$_3$:Sm$^{3+}$ samples and 5.37 – 5.42 eV for Y$_2$O$_3$:Sm$^{3+}$:Gd$^{3+}$ samples. The PL studies reveals that the emission intensity is maximum at 608 nm. After the addition of co-dopant, the position of the peak remain same but the luminescence intensity is increased by 4.21 times as compared to doped samples.

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