STRUCTURAL EVOLUTION AND SPECTRAL PROPERTIES OF CUBIC NEODYMIUM OXIDE PREPARED BY ANNEALING

K. Parimala Gandhi & N. Kavitha*

**Department of Science and Humanities, Nehru Institute of Technology, Coimbatore, Tamilnadu, India.*

Department of Science and Humanities, Nehru Institute of Engineering and Technology, Coimbatore, Tamilnadu, India.

**Corresponding author*

ABSTRACT

Nanocrystalline Nd_2O_3 was synthesised by the decomposition of the product of the reaction between neodymium Nitrate, 3-hydroxy-1-naphthoic acid and hydrazine with pH 5. The product $[Nd_2\{NZ\}_3(Hz)_4].H_2O$ (NZ = Naphthoate anion, Hz = hydrazine hydrate) was characterized by analytical, IR, UV-visible spectroscopy, magnetic moment measurement, X-ray crystallography and Thermal studies. In IR spectra the N-N stretching frequencies in the region 949 – 961 cm^{-1} unambiguously prove the bidentate bridging nature of N_2H_4 ligand. Simultaneous TG-DTA of the complex shows that the complex is stable up to 79°C and gives metal oxide as the final product at 710 °C. It is discovered that the complex coated on a glass plate forms granular neodymium oxide coating during pyrolysis in a furnace at 720 °C. It has been found that the toughening time and sintering temperature played a vital part to the arrangement of cubic neodymium oxide. The SEM- EDX and X-ray powder diffraction pattern reveals that the presence of respective metal oxides in nanosize. The Debye-Scherrer relation has been used to calculate the crystallite sizes. The kinetic parameters of the decomposition of the complex have been computed by Coats-Redfern equation.

Keywords: Nano structure; neodymium oxide; Thermal analysis; Thin film; Annealing process

INTRODUCTION

Hydrazine, NH_2 - NH_2, is the simplest diamine and is unique in its class because the N-N bond. Hydrazine is of considerable interest as ligand in view of the variety of bonding possibilities they exhibit. One possibility is that the two nitrogen atoms, whilst being incapable of bonding to the same metal atoms, thus forming polymeric chains with hydrazine bond. There have been reports in the literature of hydrazine complexes of inner transition metal ions with various carboxylic acids (Karuppannan Parimalagandhi et al., (2014). These include simple aliphatic mono and dicarboxylic acids, aromatic mono and di carboxylic acids, heterocyclic acids and naphthoxy and hydroxy naphthoic acid systems (Surender Duhan et al., (2009). Hydrazine was long thought to be a unique substance that could only be found in aqueous solutions and in the form of certain salts.

The reactivity of metal and non-metal alkoxides provides a simple and convenient method for preparation of variety of metallo-organic and non-metallo-organic compounds. The legating properties of 3-hydroxy-2-naphthoic acid containing hydroxy groups (-OH) adjacent to the carboxylic acid group (-COOH) have been extensively examined. These molecules are used as chelating agents fluorescent indicators and the manufacture of dyestuffs. Being a straightforward diamine, hydrazine functions as a neutral monodentate, bidentate bridged, and monodentate $N_2H_5^+$ cation in a variety of complexes (W. Que et al., (2002).

Rare earth oxides have been used in many fields such as catalyst carrier, optical devices, sensors, ceramic industry, photoluminescence, advanced high temperature superconductors, and integrated optics. They can moreover be utilized as an dynamic media for glass lasers (Saruchi et al., (2014). The thin films of Nd_2O_3 are used for many purposes like gas insulator, reflection coating, and protective coating. Nano crystalline Nd_2O_3 has been synthesized by various methods such as inverse microemulsion, high-boiling polyalcohol solutions, melt casting, hydrothermal sol-gel auto-combustion, chemical vapour deposition method etc. Rare earth ions are used as dopants in glasses, because it has well-defined and sharp energy levels, which serve as structural probes for the environment of the dopants. Many researchers (Surender Duhan, (2009) have carried out research work on different properties of Neodymium oxide thin films at different conditions using different deposition techniques. They possess many properties suitable for high power laser applications include low thermal expansion co-efficient, high temperature stability, large band gap and low nonlinear refractive index (S. Duhan et al., (2009).

The thermal annealing method plays an important role to alter the fundamental size controlled on Nd_2O_3 doped silica powder prepared by the sol-gel method. It was observed that the structure of Nd_2O_3 doped silica powder depends on annealing temperature (1250 °C) and time 6 hours. However, the sintering temperature in the current investigation was 600° C for two hours. It mainly supports the development of the cubic Nd_2O_3. Neodymium oxide nanocrystallites in a silica lattice with a normal measure of almost 30 nm. The Fourier transformation infrared spectroscopy (FTIR), Ultra-violet, Visible spectroscopy (UV-Visible) X-ray diffraction, Scanning electron microscopy (SEM) data are found the prepared sample. Recently, the rare earth metallic-oxide films are used in the optical filters for improving colour purity and for expanding colour reproducibility in the colour alternating current plasma display panel (D. K. Lee et al., (2002), because the strong absorption bands due to intra transitions within the 4f shell of the Nd(III) ion. The intra transition of Nd(III) ion depend on the thickness of Nd_2O_3 film. In this work, neodymium nitrate, 3-hydroxy-2-naphthoic acid and hydrazine were used as ligand for the preparation of neodymium oxide film and their characterization by IR and UV-visible spectroscopic methods, magnetic measurements, powder X-ray diffraction, SEM-EDX research, and TG-DTA analysis.

EXPERIMENTAL

Neodymium nitrate (Nd_2O_3), 3-hydroxy-2- naphthoic acid, hydrazine hydrate (N_2H_4 .H_2O) and con. HNO_3 (spg = 1.4g/ml) were used for preparation of complex.

Preparation of Neodymium oxide

Neodymium Nitrate solution [Nd_2O_3 (0.336g, 1 mmol) was dissolved in a minimum quantity of 1:1 HNO_3, evaporated to eliminate excess of acid, and dissolved in 20 mL of water] was added slowly to freshly prepared aqueous solution (60 ml) of the ligand containing hydrazine hydrate (0.2g, 4 mmol) stirring the reaction mixture at pH 5, immediately turbidity developed which turned out to be micro-crystalline solid. Following filtering, the complex was cleaned with alcohol, water, and ether before being dried. The powder form of the pure sample are coated with soda glass substrate and based on the decomposition temperature it is sintered in muffle furnace at 720° C (KSL 1600X, MTI) in air atmosphere the light violet neodymium oxide coated film was obtained. The analytical datas for the complex are, calculated: C – 40.25 %; H – 2.01 %; N - 6.03 %; N_2H_4 -13.2 %; Nd -28.6 %. Found: C – 40.53 %; H – 2.24 %; N – 6.25 %; N_2H_4 – 13.5 %; Nd – 28.5 %.

Physicochemical Techniques

Titrating against standard KIO_3 (0.025 mol L^{-1}) in Andrew's conditions yields the hydrazine concentration. Utilizing xylenol natural pointer and concentrated HNO_3 to devastate the hydrazine and natural materials and vanish the overabundance HNO_3, the sum of the metals is measured volumetrically utilizing EDTA (0.01 mol L^{-1}) (Raju B, *et al*., (2008). Several complementary methods were used to characterize the prepared sample like X-ray Diffraction (XRD), Fourier Transform Infrared spectroscopy (FTIR), Ultra-violet Visible spectroscopy (UV) and Scanning Electron Microscopy (SEM). The complex's infrared spectra were captured as KBr pellets using a Shimadzu FTIR-8201 (PC)S spectrophotometer, covering the range of 4000 to 400 cm^{-1}. The compound is insoluble in water and organic solvents, and hence their electronic absorption spectra are recorded for solid sample. Electronic absorption spectra of Nd(III) complex are obtained using a Varian Cary 5000 recording spectrophotometer. The magnetic susceptibility of the complex was measured using a vibrating sample magnetometer, Lakeshore VSM model 7410 at room temperature. The X-ray powder diffraction patterns of the complex and neodymium oxide coated glass substrate are recorded using Bruker X-ray diffractometer (model AXS D8 Advance) employing Cu-Kα radiation with nickel filter. The TG-DTA experiments are carried out using Perkin Elmer Diamond TG/DTA analyzer in air atmosphere at a heating rate of 10° C min^{-1} using 5 to 10 mg of the samples. Platinum cups are employed as sample holders and alumina as reference. The temperature range is ambient to 700 °C. The elemental analysis is carried out using an Elementar Vario ELIII CHNS elemental analyzer. Using the JEOL model JSM-6390 LV and the JEOL model JED -2300 instrument, the SEM with EDX analysis was obtained.

RESULTS AND DISCUSSION

IR Spectra

The comparison of IR spectra of neodymium complex and their oxide is shown in Figure. (1a & b). In the IR spectra of the complex the broad band observed at 3056 – 3600 cm^{-1} is assigned to the N-H stretching of hydrazine molecules. The N-N stretching in hydrazine complexes are much important in assigning the nature of its coordination. (Braibanti et al., (1968) have given a thumb rule on the basis of earlier studies to distinguish the different modes of coordination of hydrazine molecules by carefully examining the N-N stretching frequencies. On this basis the infrared frequency region between 949 – 961cm^{-1} was closely observed in the present series of complex. In the case of transition metal complexes in this region the only one sharp band at 960-981 cm^{-1} was observed which was attributed to the bidentate bridged nature of N_2H_4 moiety, and broad absorption peaks in the range of 3265 – 3299 cm^{-1} is assigned to O-H vibrations of the associated water molecule. An additional peak observed at about 596 cm^{-1} is evidence for the presence of lattice water in the complex. The COO- group coordinated to metal is found by their symmetric (C=O) and asymmetric (C=O) vibration at 1527 cm^{-1} and 1658 cm^{-1} respectively, and their difference being smaller than 200 cm^{-1} suggests that metal is coordinated bidental (R. Bazzi *et al.*, (2003). The other peaks are common with those of acid. The complex has enough stability in toluene solution to act as a precursor without containing any carbon. Solid thin film grown from this complex at

525° C consists of neodymium metal with contamination but at 710° C the complex yield thin film containing Nd_2O_3 under oxygen environment.

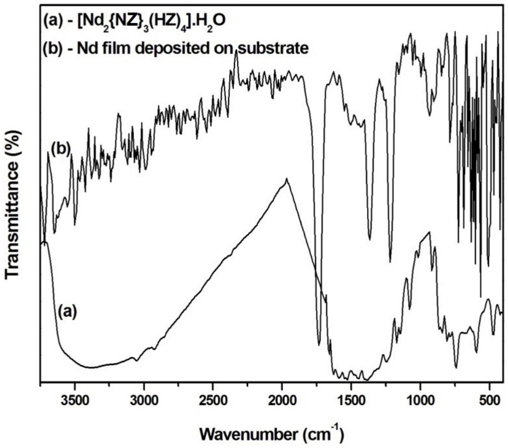

Figure.1- IR spectrum of (a). $[Nd_2\{NZ\}_3(HZ)_4].H_2O$ and (b) Nd film deposited substrate

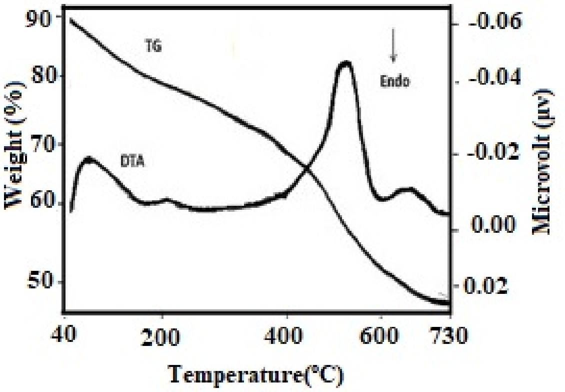

Figure.2 -TG/DTA curve of $[Nd_2\{NZ\}_3(HZ)_4].H_2O$ at a rate of 10° C/min under oxygen atmosphere

The Nd complex the peak observed at 949 cm^{-1} due to the presence of N_2H_4 in bidentate bridged nature, whereas in the Nd thin film the peaks appeared at about 933 and 903.7 cm^{-1} is due to the asymmetric mode of Si-O-Nd bond (D. K, Lee et al, (2004). However, One and Katsumata reported that asymmetric stretching mode of vibration of Si-O-Pr appears at 900 cm^{-1}. The shifting of the Si-O-Nd peak towards higher spatial frequency is a result of higher ionic radius of Nd than Pr. In Nd_2O_3 thin film the peak around 1080 cm^{-1} corresponds to the TO vibrations mode of Si-O-Si asymmetric bond. The symmetric Si-O-Si stretching or vibrational modes of ring structures are linked to the thin-film peak detected at 790 cm^{-1}. However, this summit is absent from the original complex. The peak around 470 cm^{-1} is due to bending mode vibrations of Si-O-Si. D. Mishra et al., (2004) explained the 1080 cm^{-1} position of Si-O-Si bonds in terms of strains in the Si-O-Si bridging bonds present at the surface of the pores. Pores gradually collapse as densification moves forward, causing strain relaxation and a rise in band wave number. The peak at 1080 cm^{-1} is shifted towards higher wave number (1127 cm^{-1}) which may be due to the conversion of Nd complex to Neodyimum oxide.

Electronic Spectra and Magnetic Susceptibility Measurements

The electronic spectral data for Nd (III) complex consist of number of weak bands but sharp bands due to the Laporte forbidden f-f transitions. The majority of ions are colorless and contain half-or fully-filled 4f-orbitals, meaning they lack unpaired electrons. Hence, the 4f orbitals are main source of colour of Nd(III) ions and the number of unpaired electros in these 4f-orbitals decide the colour, even though the ions have same number of unpaired electrons show different colour.

Since the compound in this instance is insoluble in organic solvents and water, solid-state electronic spectra have been observed. The electronic spectra for Nd(III) complex shows absorption at 19631, 18400, 15550, 14660, 12485 which are assigned to $^2G_{7/2}$, $^4G_{7/2}$, $^2H_{1/2}$, $^4F_{9/2}$, $^4F_{5/2}$ transitions (K. Pabhakaran et al., (2009) respectively. The maximum absorption found at visible region. The wavelength spans the visible to medium infrared spectrum, with zero absorption observed. Magnetic moment from magnetic susceptibility measurements for Nd(III) complex 3.4BM and Nd_2O_3 2.8 BM respectively, are in good agreement with the values reported . The clusters had poor magnetic properties when compared to that of complex. Because, the irregular racetrack pattern on the sputtering target combined with the soft magnetic properties of the as-deposited clusters, and the low coercivity post-annealing all lead to the conclusion that the wrong composition of clusters had been deposited (K. C. Kwaitkowski et al., (2000).

Thermal analysis

For coordination compounds, thermal degradation is a crucial tool for drawing several inferences regarding their composition and thermal stability. The thermograms (Figure. 2) reveal that the complex start losing water first and then hydrazine up to 181 ºC, showing endotherms in the range of 80 ºC to 190 ºC and wide exotherms of 190 and 502 degrees Celsius, respectively. Dehydration takes place around 100 ºC indicates that water present in the complexes is not coordinated. Through mutual heat exchange, endotherms and exotherms suppress one another, resulting in the presentation of weaker peaks. This is a frequently seen phenomena that occurs when hydrazine complexes decompose and simultaneously remove water and hydrazine. (I. K. Battisha, (2001). Then a continuous decomposition of hydrazine complexes from 502 ºC to 720 ºC corresponding to the decomposition of the remaining compound to oxide.

Our attempt to separate the intermediates was failed due to their continuous decomposition as evident from the TG. Hence, we have tried to assign the possible intermediates as observed from the TG mass losses, which are accord with the calculated mass losses. In the case of transition metal complexes, hydrazine is eliminated separately showing clear exothermic peak in the range 250 ºC to 262 ºC (H. Ono et al., (2001) forming metal hydroxy naphthoate as intermediate but the decomposition is continuous metal oxides are obtained due to evolution of nitrogen, hydrogen and carbon dioxide gases. By comparing the residue's XRD pattern, the oxides' production is verified.

Scanning Electron microscopy

(Figure. 3) shows a scanning electron microscopy image of the deposited Nd_2O_3 particles. The sem image of the final product formed after the incineration of the complex at their decomposition point, and sintering at the same temperature for about 2-3 hours. Solid thin film grown from this complex at 525 °C consists of Nd with contamination. But at 710 °C the complex yield pure Nd thin film under oxygen environment. Because Nd_2O_3 was not evenly distributed throughout the silica matrix in this film, the particles have an irregular shape and are nanosized.. The measurement from the image indicates that these are nano particle with size range from 30 – 80 nm. EDAX analysis confirms that the film contains pure Nd particles. The size of the particle can be measured by using Scherrer's formula (Coats et al., (1964) $D = K\lambda/\beta \cos\theta$, where λ is the X-ray wavelength, β is the full width of height maximum (FWHM) of a diffraction peak, where K is the Scherrer's constant of order 0.89 and θ is the diffraction angle.

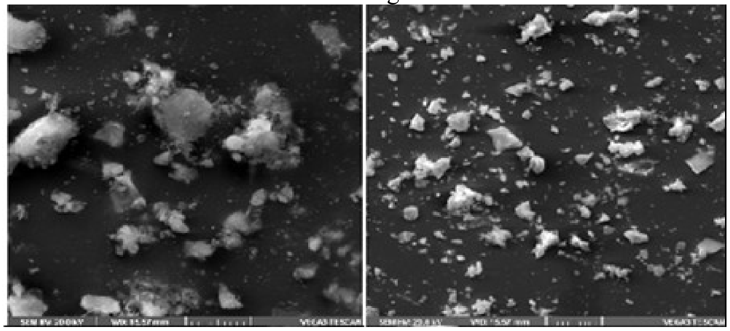

Figure.3 -SEM image of neodymium nano particles ranging from 30-80 nm deposited on soda glass substrate

XRD analysis

Xrd pattern of soda glass substrate, Nd thin film deposited on soda glass substrate. The film deposit at 710° C under nitrogen environment with the collecting angle range from 3°-60° C and Cu-Kα radiation λ = 1.5406 Å. A common formula can be used to compute the lattice parameter. (Lattice $= d\sqrt{(h^2 + k^2 + l^2)}$). The hkl values (222), (400), (440) and (622) , 2θ values 27.5°, 31.6°, 46.3° and 54.8° and corresponding d values 3.255, 2.720, 1.968 and1.676 are used for determining lattice parameter which found to be 11.2, 11.3 ,11.1 and 11.1 Å. The XRD pattern's relative peak intensities and diffraction peak locations matched the JCPDS data. The position and the integral width of x-ray diffraction peaks are determined to identify the crystalline phase which is found to be body centered cubic (Karuppannan Parimalagandhi et al., (2014).

Kinetic Studies

Dehydration (Figure. 4) kinetics of complex are followed by using TG. The parameters have been calculated using integral method developed by Coats et al., (1964). The equation used for calculation of the E and A parameter is

$$\log\left(1-\frac{\left(1-\alpha\right)^{1-n}}{T^{2}\left(1-n\right)}\right)=\log\frac{AR}{\varphi E}\left(1-\frac{2RT}{E}\right)-\frac{E}{2.303RT}$$

where A is the pre-exponential factor (S^{-1}), R is the gas constant (8.314 J.k-1mol^{-1}), E is the activation energy ($kJ.mol^{-1}$), T is the temperature (K), Ά is the percentage responded time t, n is the order of the decomposition reaction, φ is the heating rate in °C degree/min. Plotting Y versus 1/T gives a straight line for a parameter. From the slope (-E/2.303R) and intercept log AR/φE[1-(2RT/E)], E and A are calculated (Karuppannan Parimala gandhi et al., (2016). The order of the reaction, activation energy and pre-exponential factor for the dehydration and decomposition steps are 0.3 and 3, 64.14 and 107.25 KJ/mole, 10.72×10^{11} and 2.51×10^{27} (S^{-1}) respectively.

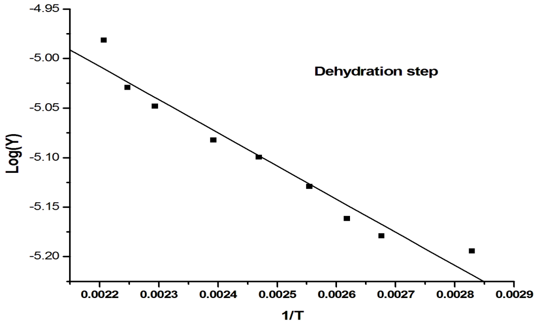

Figure. 4- dehydration step of $[Nd_2\{NZ\}_3(HZ)_4].H_2O$

Conclusion

The present work Nd_2O_3 prepared by simple synthetic procedure and characterized by physico-chemical methods such as elemental analysis and x-ray analysis. Decomposition pattern studies of the complex by TG and FTIR indicates that metallic neodymium as a major residue. Thin film having average size 30 – 80 nm of the neodymium nano particle have been deposited on soda glass substrate by slow annealing technique. It has been confirmed by SEM-EDX and XRD. Kinetic parameters can also be determined.

REFERENCES

[1] Braibanti, F. Dallavlle, M.A. Pellinghalli and E. Leporati (1968). Inorg. Chem. 7, 1430.

[2] A.W. Coats and J.P. Redfern (1964). Nature, 201 68–69.

[3] D. K, Lee, Y. Cho, S. H. Sohn and H. K. Kim, D. K, Lee, Y. Cho, S. H. Sohn and H. K. Kim (2004). Electrooptical Characteristics of Neodymium-Containing Transparent Dielectrics for Plasma Display Panel, J. Korean Phys. Soc. 45, 1236.

[4] D. K. Lee, S. M. Seo, S.G. Lee, S.H. Sohn, S. H. Park and H. M. Kim (2002). Optical properties of inorganic $(SiO_2)_{1-x}(Nd_2O_3)x$ alloy films for the color filter of plasma display panel, Appl. Phys. Lett.80, 983. https://doi.org/10.1063/1.1448662

[5] G. Cao (2004). Nanostructured and Nanomaterials, Imperial College Press, London, *J. Am. Chem. Soc.* 126, 44, 14679. https://doi.org/10.1021/ja0409457

[6] H. Ono, and T. Katsumata (2001). Interfacial reactions between thin rare-earth-metal oxide films and Si substrates, Appl. Phys. Lett. 78, 1832. http://dx.doi.org/10.1063/1.1357445.

[7] I. K. Battisha (2001). Structural and Optical Studies of Nano-structure Monolithic Silica-Gel Derived Glasses Containing Nd3+, Egypt. J. Sol. 24, 5.

[8] K. C. Kwaitkowski, C. M. Lukehart (2000). In Handbook of Nanostructured Materials and Nanotechnology, Edited H. S. Nalwa, Academic: New York.

[9] K. Pabhakaran, P. K. Ojha and S. C. Sharma (2009). An, Sucrose combustion synthesis of nanocrystalline yttrium aluminium garnet ($Y_3Al_5O_{12}$) powder, J. Am. Ceram. Soc. 108, 4. https://doi.org/10.1179/174367608X362403

[10] Karuppannan Parimalagandhi & Sundararajan Vairam (2014). Kinetics and Thermal Decomposition of Tetrahydrazinelanthanum (III) 2-hydroxy-1-naphthoate, Orient. J. Chem., Vol. 30(4), 1957-1963. http://dx.doi.org/10.13005/ojc/300458

[11] Karuppannan Parimalagandhi, Thathan Premkumar, Sundararajan Vairam (2016). A general method for preparing lanthanide oxide nanoparticles via thermal decomposition of lanthanide(III) complexes with 1-hydroxy-2-naphthoic acid and hydrazine ligands, Journal of Physics and Chemistry of Solids., 96-97, 60–67. http://dx.doi.org/10.1016/j.jpcs.2016.04.011.

[12] R. Bazzi, M. A. Flores-Gonzales, C. Louis, K. Lebbou, C. Dujardin, A. Brenier, W. Zhang, O. Tillement, E. Bernstein, and P. Perriat (2003). Synthesis and luminescent properties of sub-5-nm lanthanide oxides nanoparticles, J. Lumin. 102, 445.https://doi.org/10.1016/S0022-2313(02)00588-4

[13] Raju, B., Sivasankar, B.N (2008). Spectral, thermal and X-ray studies on some new Bis-hydrazine lanthanide(III) glyoxylates. J Therm Anal Calorim 94, 289–296. https://doi.org/10.1007/s10973-007-8953-3

[14] S. Duhan and P. Aghamkar (2009). Interfacial Reactions and Cubic Neodymium Oxide Formation in Low Dispersed Nd_2O_3–SiO_2 System by Wet Chemical Method, Chinese Phys. Lett. *26(1).* https://doi.org/10.1088/0256-307X/26/1/016106.

[15] S. Duhan, and P. Aghamkar (2009). Interfacial Reactions and Cubic Neodymium Oxide Formation in Low Dispersed Nd_2O_3–SiO_2 System by Wet Chemical Method, Chin. Phys. Lett. 26, 1. http://dx.doi.org/10.1088/0256-307X/26/1/016106

[16] Saruchi, Surbhi, Praveen Aghamkar,and Sushil Kumar (2013). Structural investigations on Nd-doped silica nanocomposites: Effect of sintering temperature and dopant concentration, Adv. Mat. Lett. 4, 78. https://doi.org/10.1080/09500839.2014.939734

[17] Surender Duhan (2009). Effect of sintering time on particle size of rare earth compounds (R = Nd) prepared by wet chemical method Indian. J. Pure and Appl Phys. 47, 872.

[18] Surender Duhan, Sunita Devi and M. Singh (2009). Structural characterization of Nd-doped in silica host matrix prepared by wet chemical process, Journal of Rare Earths, 27(1), 83-86. https://doi.org/10.1016/S1002-0721(08)60196-9

[19] W. Que, H. Hu, L. H. Gan, and G. R. Deen (2002). Preparation and luminescence properties of neodymium (iii) oxide nanocrystals dispersed in sol-gel titania/(γ-glycidoxypropyl) trimethoxysilane composite thin films, J. Mater. Res. 17, 1399. https://doi.org/10.1557/JMR.2002.0208.