Microwave assisted sintering of Nanostructured Infrared-Transparent $Nd_{0.1}Y_{1.9}O_3$ ceramics Synthesized by a Modified Combustion Technique

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Abstract

Synthesis of nano particles of $Nd_{0.1}Y_{1.9}O_3$ ceramics (~15nm) by a single step auto-igniting combustion technique, followed by microwave sintering to optimum density, and their remarkable infrared transmission characteristics are presented in this paper. The XRD pattern of the as prepared sample clearly indicates that the Nd^{3+} ions are effectively replacing Y^{3+} ions in the yttria cubic structure and it matches very well with the JCPDS file no-89-5591. The size of the crystallites was calculated using Scherrer formula and they found to be in the size range of 10-19 nm and the average size of the crystallites was 15 nm. The HRTEM analysis confirms the nano nature and the well-defined lattice structure of the sample. The UV-Visible and FTIR spectroscopy were effectively used to characterise the powder and to obtain the transmittance properties of the sintered samples. Microwave heating was successfully employed to sinter the sample pellets. A soaking duration of 20 minutes at 1500ºC yielded well sintered (98.8%) translucent pellet with reduced average grain size of 500nm and it showed a transmittance of 77% in the UV-Visible region and 78% in the mid infrared region. Microwave assisted sintering of the combustion synthesized powder is therefore a promising fabrication technique, especially for infrared transparent ceramics, which considerably reduces the sintering temperature, soaking duration, the grain size and enhances the transmittance properties. These results clearly indicate that by prudently tuning the concentration of the additives, the IR transmittance properties can be improved and they can be used very effectively for the fabrication of infrared transparent windows and domes.

Keywords : Microwave sintering, combustion synthesis, infrared transparent

1. Introduction

Infrared transparent ceramics found to have applications as windows in homing missiles. In addition to the strategic defense and space applications they also have large spectra of civilian applications [1-6]. In most of the cases cubic phase of transparent ceramics are selected by the researchers due to the absence of birefringence. Cubic Y_2O_3 is a potential infrared transparent candidate due to its large infrared cut-off, high corrosion resistance, absence of birefringence, high mechanical strength, high thermal stability and low emissivity at elevated temperatures [1, 7-11]. A large number of factors adversely affect the efficacy of yttria as an infrared transparent window. The sintering temperature of yttria is above 2000ºC[12,13]. But there are reports in which nano phase yttria is sintered at a comparatively low temperature of 1700ºC by different methods where the fabrication methods are cumbersome[14-16]. Nanostructured high quality starting powder may enhance the mechanical properties without affecting the infrared transmittance in the mid IR range. In addition to the

quality of the starting powder, doping and fast sintering mechanisms effectively improve the performance of infrared windows.

A number of fabrication methods [17-22] have been developed successfully so far to synthesize ultrafine nanostructured polycrystalline Y_2O_3. Among them combustion synthesis is evolved as the economic and efficient method in terms of the cost, time and the complexities in the synthesis of nanomaterial. In the present work, a modified combustion technique is used to synthesize nano structured $Nd_{0.1}Y_{1.9}O_3$. The modified combustion technique is a relatively simple method viz. with the omission of high temperature calcinations for prolonged duration; we could obtain phase pure nano particles of extremely small size (5-25 nm) and further compacted to an optimum density at a much lower temperature with high thermal stability and good transparency to infrared radiation using microwave heating technique.

In this paper we report the synthesis of nanostructrured poly-crystalline $Nd_{0.1}Y_{1.9}O_3$ ceramics by an auto-ignited combustion technique [23]. The structure, vibrational spectra and surface morphology of the combustion synthesized powder are also studied and presented. The sintering behaviour of compacted pellets using resistive heating and the transmittance of infrared radiations through the sintered pellets in the UV-Visible and mid infrared ranges are also reported.

2. Experimental Procedure

A single step auto-igniting combustion synthesis is used to prepare nano structured $Nd_{0.1}Y_{1.9}O_3$ [23-26]. Stoichiometric amount of high purity $Y(NO_3)_3.6H_2O$ and Nd_2O_3(99.99%, Alfa Aesar, USA) were dissolved in double distilled water to make a clear solution. Citric acid was then added to it as a complexing agent. Amount of citric acid is calculated based on total valence of the oxidizing and the reducing agents for maximum release of energy during combustion[26]. Nitric acid was used as oxidising agent and ammonia as fuel and the pH of the solution was monitored till it became 7. The solution containing the precursor mixture was heated using a hot plate at 250 ºC in a ventilated fume hood. The solution boils on heating and undergoes dehydration accompanied by foam. The foam then ignites by itself on persistent heating giving voluminous and fluffy product of combustion.

The as-prepared nanopowders obtained from the combustion process are characterized by different powder characterization techniques. As-prepared samples are characterized by X-ray diffractometer (Xpert-pro) with Cu Kα radiation in the range of 20–80º in steps of 0.0840 for the determination of crystalline structure and phase of the nanomaterials. The average crystallite size is estimated for all the samples from Scherrer's equation. The Wiliamson-Hall plot is used for studying lattice strain in the sample. The absorption spectrum of as-prepared sample is recorded using a Shimadzu spectrophotometer (UV-1700). The uv–vis spectra are recorded to resolve the correlation between the grain size and absorption edge of the nanoparticles. Additional information regarding the phase purity and the presence of any inorganic impurity are obtained using FTIR spectroscopy using Fourier Transform Infrared spectrometer (FTIR, Perkin elmer spectrum 2) in the range 400-4000 cm^{-1} using ATR mode. Particulate properties of the combustion product are examined using high resolution transmission electron microscopy (TEM, Model-Hitachi H600 Japan) operating at 200 kV. The samples for Transmission Electron Microscope (TEM) are prepared by ultrasonically dispersing the powder in methanol and allowing a drop of this to dry on a carbon-coated copper grid.

The pure white powder is uniaxially compacted in to pellets in a 14mm diameter steel die at 200 MPa. The pellets are heat treated at 600 °C for half an hour to remove the binder and absorbed gases. The pellets are sintered at 1500 °C for a soaking time of 20 minutes in a in a microwave furnace with silicon carbide susceptors (VBCC/MF/86,VB Ceramics Consultants, India). The morphological investigations of the sintered pellets are performed in Scanning Electron Microscope (SEM, Jeol 6390LV). The transmittance of radiation in the uv-visible and in the IR range is measured using UV-Vis and FTIR spectrometers.

3. Results & Discussion

Figure 1 shows the powder XRD patterns of as-synthesised $Nd_{0.1}Y_{1.9}O_3$. All the peaks are indexed for a body centred cubic structure of Y_2O_3 which agrees very well with the XRD data reported in JCPDS file no-89-5591. The XRD pattern of the as prepared sample matches very well with that of pure yttria which clearly indicates that Nd^{3+} ions are effectively replacing Y^{3+} ions in the yttria cubic structure. Thus the XRD results confirm the formation of pure cubic $Nd_{0.1}Y_{1.9}O_3$ nanoparticles without any post annealing or calcination process.

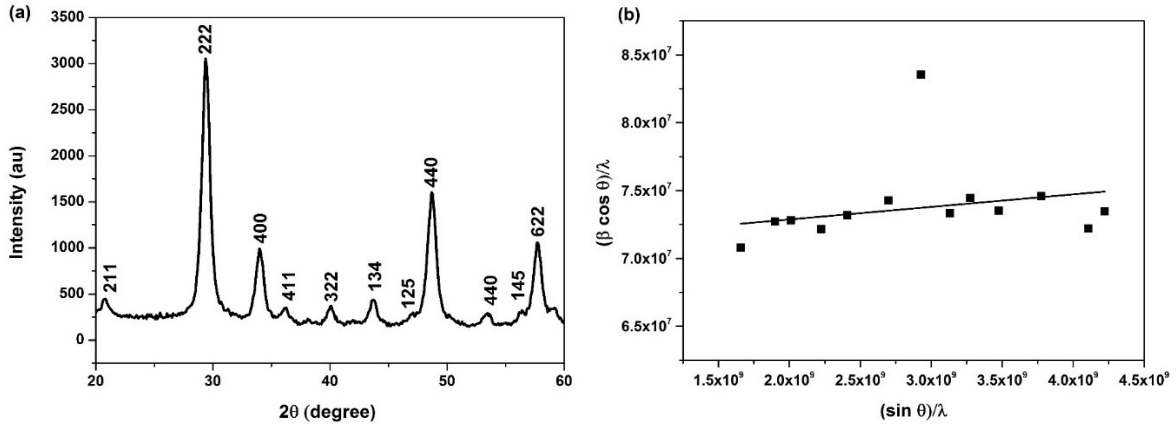

Figure 1: (a) XRD pattern of as prepared nano $Nd_{0.1}Y_{1.9}O_3$ **(b)** Hall-Williamson plot of as prepared nano $Nd_{0.1}Y_{1.9}O_3$

The crystallite size calculated using Scherrer formula [27] and for the major (*222*) peak, it is found to be 12.4 nm and the interfacial spacing corresponding to the plane is 0.3040 nm which matches very well with the JCPDS value of 0.3615 nm for the same plane. The particles were found to be in the size range of 10-19 nm and the average size of the crystallites is 15 nm. Hence the modified auto-igniting combustion method offers an excellent and economic way for the preparation of phase pure $Nd_{0.1}Y_{1.9}O_3$ nano powder.

The extent of line broadening in the diffraction pattern due to the strain, which is caused by the non-uniform displacement of the atoms with respect to their reference lattice position, could be identified by Hall–Williamson (W-H) method [28]. In this method, the reciprocal peak width $\beta cos\theta/\lambda$ is plotted against the reciprocal lattice distance $sin\theta/\lambda$, and the resulting plot was linearly fit. Figure 1(b) shows the Hall–Williamson plot for the $Nd_{0.1}Y_{1.9}O_3$ nanoparticles. The reciprocal of y intercept which was a measure of particle size obtained from this plot was 14.1 nm. The lattice strain constant η is proportional to the slope of the line, and from this plot the

estimated value of η is 9.24×10^{-4}. The positive slope of the line indicates that strain is tensile strain and even though it was very small also a component contributing to the broadening of peaks in the XRD pattern.

Figures 2(a) and (b) are the HRTEM images of the as-prepared powder sample. From the distinctly visible grain in figure 2(a) the grain size was calculated as 12.0 nm corresponding to the (*222*) plane of cubic crystal structure of $Nd_{0.1}Y_{1.9}O_3$ and was found to be in good agreement with the interfacial spacing for the same plane obtained from X-ray diffraction analysis.

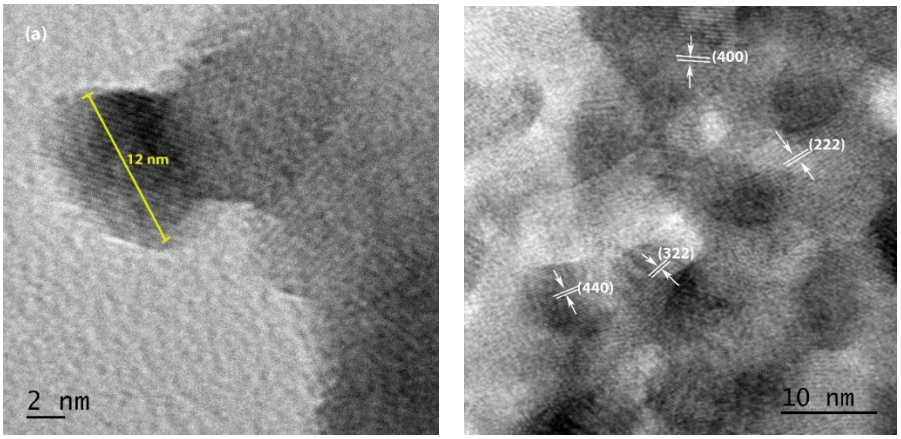

Figure 2 :(a) HRTEM image of a single grain and (b) HRTEM image of different crystallographic planes

Structural analysis in detail was done using FT IR shown in figure 3. The graph confirms that the $Nd_{0.1}Y_{1.9}O_3$ powder transmits IR in the range 2.5µm-20µm. The peak at 564 cm^{-1} corresponds to metal-oxide stretching vibration [18,19,29,30]. Broad peak around 3400 cm^{-1} correspond to O-H stretching modes of water adsorbed by the powder. No other absorption peaks are observed in this range which shows that no residual nitrate or organic matter is present in the precursor powder.

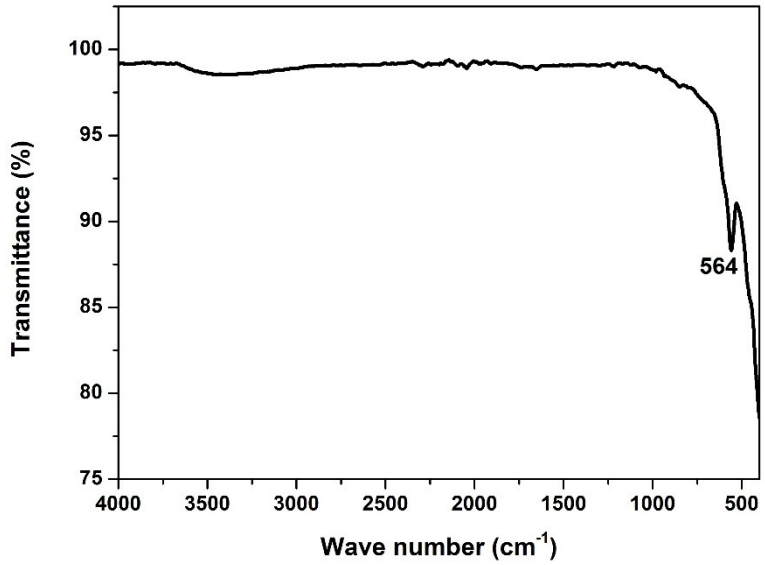

Figure 3 : FTIR transmittance spectrum of as synthesised $Nd_{0.1}Y_{1.9}O_3$

The UV-visible spectrum was recorded in the range 200-800nm and is shown in figure 4. It is observed that the sample shows maximum absorption in the UV region and decreases towards the visible region. The maximum absorption is at 242 nm, such materials were potential candidates for UV filters, which filter higher energies of the ultraviolet spectrum from 10nm to 120nm which are ionising and also find application as microwave filters. From the absorption spectrum it is clear that the sample exhibit transmittance of above 90% in the visible region. The properties of poor transmittance in the UV region but high transmittance in the Vis–NIR regions makes nano $Nd_{0.1}Y_{1.9}O_3$ an excellent material for screening off the hazardous UV portion of the electromagnetic spectrum . The optical band gap energy could be determined from the excitonic peak at 205 nm wavelength using the equation $E=hc/\lambda$ where h is the Plank's constant, c is the velocity of electromagnetic radiation and λ is the wavelength corresponding to the absorption. The corresponding band gap for the wavelength 205 nm is 6.05 eV. The refractive index of the sample can be calculated from the band gap [31,32].

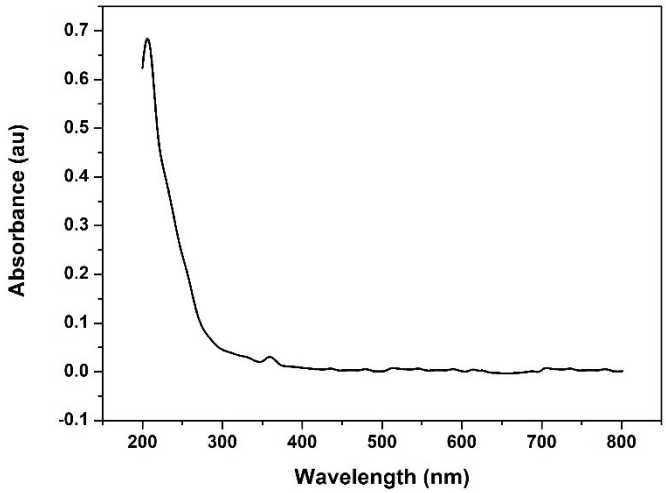

Figure 4 : UV-Visible absorption spectrum of as synthesised $Nd_{0.1}Y_{1.9}O_3$

Sintering behaviour was studied on the disc shaped yttria pellets using a silicon carbide susceptor aided microwave furnace. The relative densities of sintered pellets at different sintering temperatures for a soaking time of 20 minutes are calculated. In the microwave furnace the pellets were heated at a constant rate of 40 $^oCmin^{-1}$ and were sintered to 98.8 % of theoretical density by holding for two hours at 1500^{o}C, which is considerably low sintering temperature relative to the recent reports[33].

The sintered pellet which achieved 98.8 % of the theoretical density was hand polished and thermally etched at 1400^{o}C for 1 hour in air. The surface morphology of the sintered sample was studied using Scanning Electron Microscopy. The SEM micrograph of the $Nd_{0.1}Y_{1.9}O_3$ ceramics after the initial polishing is shown in Figure 5. The grain boundaries were sharp with minimum porosity without showing any abnormal growth or melting at the grain boundaries and the full-grown grains are in the size range of 100-700 nm. The grain sizes are accurately measured using the Image J software and the average grain size is found to be 600 nm.

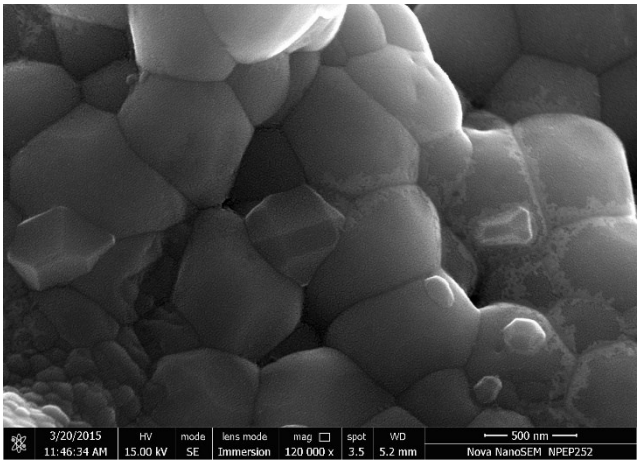

Figure 5: SEM micrograph of conventionally sintered $Nd_{0.1}Y_{1.9}O_3$ pellet sintered to 98.8 % of theoretical density

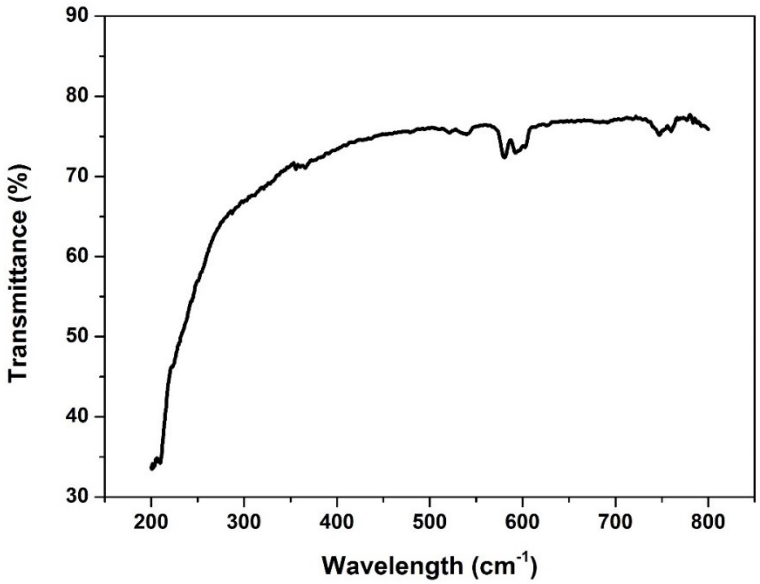

Figure 6: UV-Visible transmittance of the $Nd_{0.1}Y_{1.9}O_3$ pellet sintered to 98.8% theoretical density

In the absence of absorption or scatter the transmittance of a body is given by the relation,

$$t = \frac{2n}{n^2 + 1}$$

where n is the refractive index. The refractive index is one of the fundamental properties of a material which is closely related to the electronic polarisability and local field inside the material. Reddy et al.[31,32] formulated an empirical relationship between the refractive index and band gap energy,

$$E_g e^n = 36.3$$

Using the above relation the refractive index of the present sample with band gap energy of 6.05 eV is calculated as 1.79. The theoretical limit of transmittance through the sintered pellet according to the relation is calculated as 85.11%. The pellets after the initial hand polishing followed by polishing using diamond pastes of fine grades in a self-designed lapping

and polishing machine and the final mirror polished pellets are used for the transmittance studies. The UV-Visible spectrum of the sintered pellet of density 98.8% of the theoretical density and thickness 0.5mm is shown in the figure 6. The pellet shows a maximum transmittance of 77.0% at 800 nm and is found to be translucent.

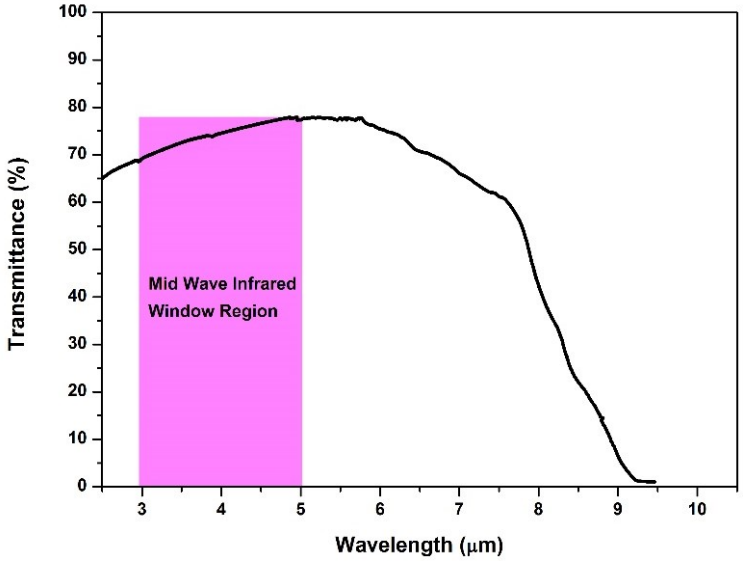

Figure 7: IR spectrum of $Nd_{0.1}Y_{1.9}O_3$ pellet sintered to 98.8% of theoretical density

The IR spectrum of the conventionally sintered sample in figure 7 shows that it has a maximum transmittance of 78.0 % at 5 μm . The good transmittance in the Mid IR range makes it ideal for infrared transparent windows and domes.

4. Conclusions

A single step auto-igniting combustion synthesis is used to prepare nano structured $Nd_{0.1}Y_{1.9}O_3$ X-Ray Diffraction (XRD) analysis of the as prepared powder confirms the formation of phase pure cubic $Nd_{0.1}Y_{1.9}O_3$ nanoparticles . All the peaks in the XRD were indexed to a body centred cubic structure with a calculated lattice parameter a=10.53Å agreeing very well with the XRD data reported in Joint Committee on Powder Diffraction Standards (JCPDS) file no. 89-5591. The XRD analysis and High Resolution Transmission Electron Microscopic(HR-TEM) studies reveal that the average crystallite size is ~15 nm and the lattice planes are well defined. Fourier transform Infrared spectrum of the as prepared sample is recorded in the range 400-4000 cm^{-1} .The vibrational spectroscopic studies confirms the structure of the sample. The absorption spectra of the as prepared $Nd_{0.1}Y_{1.9}O_3$ is measured in the range 200-800nm and it shows that the material absorbs heavily in the shorter wavelength region of the ultraviolet spectrum and transmit long wavelength uv and visible light and hence found applications in the filters and sensors of UV radiations. The pure white $Nd_{0.1}Y_{1.9}O_3$ powder is uniaxially compacted in to pellets in a 14 mm diameter steel die and sintered to 98.8% theoretical density without any sintering additives or applying pressure at 1500 ºC for 20 minutes in a microwave furnace. The SEM micrograph gives the surface morphology of the well sintered pellet and from the SEM it is found that the average grain size is ~600nm. The transmission spectrum of the sintered pellet in the UV-Vis region reveals that the material is showing 77.0% of transmittance in the visible region and 78% in the Mid IR region. The better

transmittance of the pellets attribute to the quality of the nano powder synthesised by the modified combustion technique, high sintered density with minimum porosity and the smaller grain size of the sintered pellet. The results clearly indicate that the ultra fine $Nd_{0.1}Y_{1.9}O_3$ nanopowder synthesized by the modified auto-igniting combustion technique synthesised using single step combustion method followed by resistive heating can be used very effectively for the fabrication of improved infrared transparent windows and domes.

Acknowledgments

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