Effect microwave sintering in enhancing the infrared transmittance properties of combustion synthesized nanostructured $\text{Y}_2\text{O}_3$ ceramics comprising $\text{La}^{3+}$ ion in the matrix

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Abstract

Synthesis of nano particles of $\text{La}^{3+}$ ion substituted $\text{Y}_2\text{O}_3$ ceramics (~16nm) 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 $\text{La}^{3+}$ ions are effectively replacing $\text{Y}^{3+}$ ions in the yttria cubic structure and it matches very well with the JCPDS file no-89-5591. As the percentage of $\text{La}^{3+}$ increases a slight increase in lattice parameter was observed. The size of the crystallites were calculated using Scherrer formula and they found to be in the size range of 10-20 nm and the average size of the crystallites was 16 nm. The phase purity and nano nature of the crystallites were confirmed using HRTEM. The UV-Visible and FTIR spectroscopy were effectively used to characterise the powder and to obtain the transmittance properties of the sintered samples. The pellets with green density 52% of the theoretical density were sintered using a microwave furnace. The pellets achieved 99% of the theoretical density at 1520°C for a soaking duration of 20 minutes. The pellets were translucent and the SEM analysis revealed that they were well sintered with reduced average grain size of ~430nm. The pellet showed an enhanced transmittance of 77% in the UV-Visible region and 72% in the mid infrared region. The transmittance properties shown by the pellets are superior to those in the case of pure $\text{Y}_2\text{O}_3$ and is due to the superior powder quality and the fast uniform densification via microwave sintering. 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.

Keywords: Microwave sintering, Infrared transmittance, Combustion synthesis

1. Introduction

Polycrystalline infrared transparent ceramics found to have a large spectrum of applications [1-3]. The research in the field of nanostructured polycrystalline infrared transparent ceramics is in its blooming stage due to its increased demand in the strategic defence and space missions. Among various polycrystalline ceramics yttria($\text{Y}_2\text{O}_3$) ceramics have excellent properties required for good infrared transparent window materials, like high thermal conductivity and absence of birefringence [1], high thermal shock resistance [4], low dielectric loss with temperature [5], moderate refractive index and low thermal expansion coefficient [1], high melting point [6], greater hardness [7], low emissivity at elevated temperatures [8] and high transparency in the visible and infrared range [4]. The desired mechanical, thermal and electrical properties, in addition to the high infrared cut-off make it ideal for IR windows and protection domes used in strategic applications.
The major challenge in the fabrication of infrared transparent window is the sintering of the sample to high density without compromising the transmittance properties. In most of the cases very high sintering temperature is required for the densification of the nanostructured polycrystalline sample, due to which the grain size increases and adversely affect the transmittance and mechanical properties.

In the present work we use a modified combustion technique to synthesize nano structured La$_{0.15}$Y$_{1.85}$O$_3$. The modified combustion technique used in the present study is a relatively simple method viz. the omission of high temperature calcinations for prolonged duration, we could obtain phase pure nano particles of extremely small size (10-20 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. The structure, vibrational spectra and surface morphology of the combustion synthesized powder are also studied and presented. The sintering behaviour of compacted pellets using microwave heating and compared it with that of resistive heating. The transmittance of infrared radiations through the sintered pellets in the UV-Visible and mid infrared ranges are also reported.

2. Experimental Procedure

Nanostructured La$_x$Y$_{2-x}$O$_3$ (where x=0.05,0.10,0.15,0.20 and 0.25) was prepared using a single step auto-igniting combustion synthesis [9-11]. Stoichiometric amount of high purity Y (NO$_3$)$_3$.6H$_2$O (99.99%, Alfa Aesar, USA) dissolved in double distilled water and La$_2$O$_3$ (99.99%, Alfa Aesar, USA) dissolved in nitric acid were mixed to make a clear solution. Amount of citric acid, which is used as the complexing agent was calculated based on the total valence of the oxidizing and the reducing agents for maximum release of energy during combustion [12,13]. Nitric acid was used as the 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°C 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 phase purity and the crystalline nature of the as prepared La$_x$Y$_{2-x}$O$_3$ were analysed using different powder characterisation techniques. As-prepared samples were characterized by X-ray diffractometer (Xpert pro, Philips, the Netherlands) with Cu Kα radiation in the range of 20–60° in steps of 0.0840 for the determination of crystalline structure and phase of the nanomaterials. The average crystallite size was calculated using the Scherrer formula [14] D=0.9λ/β cosθ where λ is the wavelength of CuKα radiation, β is the full width at half maximum, and θ is the Bragg’s diffraction angle. The nano particulates were examined using high resolution transmission electron microscopy (H600, Hitachi, Japan) operating at 200 kV. The samples for Transmission Electron Microscope were prepared by ultrasonically dispersing the powder in methanol and allowing a drop of this to become dry on a carbon-coated copper grid. The HRTEM image is analysed using imageJ software to obtain the d-spacing and the crystallite size. Additional information regarding the phase purity and the presence of any inorganic impurity was obtained from FTIR spectroscopy taken using Fourier Transform Infrared spectrometer (Spectrum 2, Perkin-Elmer, Singapore) in the range 400-4000 cm$^{-1}$ using the ATR method. The transmission spectrum of as-prepared samples of yttria nanoparticles was recorded using a spectrophotometer (UV-1700, Shimadzu, Singapore). The refractive index of the sample is calculated from the transmission spectrum. The theoretical limit of transmittance in the UV-Visible range for a well sintered pellet using a powder with refractive index n is
estimated according to the relation $T = 2n/(1+n^2)$, where $n$ is the refractive-index [1]. The as prepared powder was uniaxially compacted into pellets in a 14 mm diameter steel die at 200 MPa using a hydraulic press. The sintering behaviour of the samples were studied using microwave heating and the results were compared with that of resistive heating. The sintering of the disc-shaped pellets were carried out in a microwave furnace with silicon carbide susceptors (VBCC/MF/86, VB Ceramics Consultants, India). In the microwave furnace, microwave heating was realized using a pair of 2.45GHz magnetrons of 1.1KW each. The experimental density of the sintered pellets was calculated using the Archimedes principle. The surface morphological studies of the sintered pellets were performed with a Scanning Electron Microscope (NPEP252, Nova nanosem, USA). The SEM image is analysed using imageJ software to obtain the grain size distribution curve. The pellet used for SEM analysis were further subjected for lapping and polishing using diamond paste of fine grades in a self-designed lapping and polishing machine. These mirror polished 0.5 mm thick pellets were used for the transmittance studies. The transmittances of radiation in the UV-visible and in the IR range were measured using UV-Vis and FTIR spectrometers.

3. Results and Discussion

The phase purity of the crystallites of the as prepared powder was investigated in detail using the X-ray diffraction technique.

![XRD pattern](image)

**Figure 1.** XRD pattern of $La_xY_{2-x}O_3$ (where $x = 0, 0.05, 0.10, 0.15, 0.20$ and $0.25$)

Fig. 1 shows the X-ray diffraction patterns of $Y_2O_3$ and $La_xY_{2-x}O_3$ (where $x=0.05, 0.10, 0.15, 0.20$ and $0.25$). All the peaks corresponds to the cubic phase of yttria and indexed using JCPDS-895591. No other peaks were observed which clearly indicate that $La^{3+}$ ions are effectually replacing $Y^{3+}$ ions in the yttria cubic structure. But the ionic radius of $La^{3+}$ (1.032 Å) is larger than that of $Y^{3+}$ (0.90 Å) ions [15] and resulting increase in d-spacings which is evident from the shift of the diffraction peaks to the lower 20 values as indicated by
the reference line in Fig.1. Table 1 shows the variation in d-spacing and cell parameters for the (222) peak with La\(^{3+}\) ion concentration. The shift in peaks towards lower 2θ values were also reported in \(\text{Y}_2\text{O}_3/\text{La}_2\text{O}_3\) system with increase in calcination temperature due to the expansion of \(\text{Y}_2\text{O}_3\) lattice along with the lanthanum ion penetration [16]. The average crystallite size calculated using Scherrer formula is 16 nm for the sample \(\text{La}_{0.15}\text{Y}_{1.85}\text{O}_3\).

| \(\text{La}_x\text{Y}_{2-x}\text{O}_3\) | d-spacing (Å) | Cell parameter(Å) |
|---------------------------------|---------------|-------------------|
| \(x = 0\)                      | 3.0601        | 10.604            |
| \(x = 0.05\)                   | 3.0639        | 10.613            |
| \(x = 0.10\)                   | 3.0657        | 10.620            |
| \(x = 0.15\)                   | 3.0693        | 10.632            |
| \(x = 0.20\)                   | 3.0722        | 10.642            |
| \(x = 0.25\)                   | 3.0767        | 10.658            |

Table 1. Change in d-spacing and cell parameter corresponding to the (222) peak with La\(^{3+}\) ion concentration

As the concentration of La\(^{3+}\) ions increase the lattice distortion increases[17] and the peaks get broadened due to the lattice strain factor in addition to the size effects. The suitable composition for the application as infrared transparent window is found to be \(x=0.15\) because the presence of La\(^{3+}\) above that composition will adversely affect the thermal conductivity of the sample so we limit our studies to \(\text{La}_{0.15}\text{Y}_{1.85}\text{O}_3\).

Figure 2: HRTEM image of different crystallographic planes

Figure 2 shows the HRTEM image of the as-prepared powder sample. Even though the powder is slightly agglomerated the crystallographic planes are well defined and they are in good agreement with the XRD data. The d-spacing corresponding to the (222) plane of cubic crystal structure of \(\text{La}_{0.15}\text{Y}_{1.85}\text{O}_3\) is 3.0691 Å.

Phase purity of the sample was confirmed using FTIR spectrum shown in figure 3. The transmittance plot confirms that the \(\text{La}_{0.15}\text{Y}_{1.85}\text{O}_3\) powder transmits IR in the range 2.5µm-20µm. The peak at 562 cm\(^{-1}\) corresponds to Y-O stretching [18-21]. Broad peak around 3400 cm\(^{-1}\) and 1661 cm\(^{-1}\) correspond to O-H stretching and H-O-H bending modes of water adsorbed by the powder. Peaks at 1510 cm\(^{-1}\) and 1410 cm\(^{-1}\) are assigned to the asymmetric and symmetric vibrations of carboxylate group formed during the combustion process. 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 $\text{La}_{0.15}\text{Y}_{1.85}\text{O}_3$

The UV-visible spectrum was recorded in the range 200-800 nm and is shown in figure 4. It is observed that the sample shows maximum transmission in the visible region which decreases towards the UV region. The absorption edge is at 225 nm. The heavy absorption in the high energy end of the UV region makes the sample a potential candidate for UV filters, which filter higher energies of the ultraviolet spectrum from 10 nm to 120 nm which are ionising and it also find application as microwave filters. The optical band gap energy could be determined by extrapolating the wavelength of the onset absorption in the UV region and using the intercept in the wavelength axis in the equation $E=\frac{hc}{\lambda}$ where $h$ is the Plank’s constant, $c$ is the velocity of electromagnetic radiation and $\lambda$ is the wavelength corresponding to the absorption. The corresponding band gap for the wavelength 225 nm is 5.55 eV.

Sintering behaviour was studied on the disc shaped $\text{La}_{0.15}\text{Y}_{1.85}\text{O}_3$ pellets using a conventional furnace having molybdenum heating elements. The relative densities of sintered pellets at different sintering temperatures for a soaking time of two hours were calculated. In conventional heating furnace the pellets were heated at a constant rate of 10 °C min$^{-1}$ and were
sintered to 98.8% of theoretical density by holding for two hours at 1590°C is found to be the lowest value of sintering temperature of pure nano \( \text{La}_{0.15}\text{Y}_{1.85}\text{O}_3 \) using conventional sintering methods without any additives or application of pressure, reported so far. To improve the sintering strategy, microwave sintering was effectively utilized to densify the sample pellet. Being a low dielectric loss material susceptor aided microwave sintering was used. The pellets were sintered to 99% of the theoretical density at a considerably low temperature of 1520°C by holding it for just 20 minutes. The relative density achieved by the pellet at different temperature during the course of study is shown in figure 5. It is clear from the figure that at lower temperature there is no much difference in the densification pattern of the sample. But at higher temperature the microwave absorption of the sample increases which is evident from the remarkable enhancement in densification after 1200°C during microwave sintering.

![Graph showing variation of relative density with sintering temperature](image)

**Figure 5**: Variation of relative density of \( \text{La}_{0.15}\text{Y}_{1.85}\text{O}_3 \) with sintering temperature

![SEM micrographs of pellets](image)

**Figure 6**: (a) SEM micrograph of conventionally sintered \( \text{La}_{0.15}\text{Y}_{1.85}\text{O}_3 \) pellet and (b) microwave sintered \( \text{La}_{0.15}\text{Y}_{1.85}\text{O}_3 \), grain size distribution is shown inset.

The sintered pellets were hand polished and thermally etched at 1440°C for 1 hour in air. The surface morphology of the sintered sample was studied using Scanning Electron Microscopy. The SEM micrograph of the \( \text{La}_{0.15}\text{Y}_{1.85}\text{O}_3 \) ceramics after the initial polishing and etching is shown in Figure 6. The pellet sintered via resistive heating is shown in figure 6(a). 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 0.6 – 1.8 µm. The grain sizes are accurately measured using the Image J software. Figure 6(b) shows SEM micrograph of microwave sintered La$_{0.15}$Y$_{1.85}$O$_3$ with 99% of theoretical density from which it is evident that the grain sizes are considerably low compared to that in pellet sintered via resistive heating and they lie in the size range 0.1 – 1 µm. and the average grain size for the entire distribution is 0.43µm. In microwave sintering a substantial reduction in the size of the grain is observed. The reduced grain size and reduced porosity may enhance the transmittance properties of the sample to a greater extent [22].

Figure 7: UV-Visible transmittance of the La$_{0.15}$Y$_{1.85}$O$_3$ pellet sintered to 99% theoretical density via microwave heating.

Figure 8: IR spectrum of La$_{0.15}$Y$_{1.85}$O$_3$ pellet sintered via microwave heating to 99% of theoretical density

In the absence of absorption or scatter the transmittance of a body is given by the relation,
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.\[23\] formulated an empirical relationship between the refractive index and band gap energy,

\[ E_g e^\frac{\omega}{n} = 36.3 \]

Using the above relation the refractive index of the present sample with band gap energy of 5.81eV is calculated as 1.83. The theoretical limit of transmittance through the sintered pellet according to the relation is calculated as 84.1%. 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 99% of the theoretical density and thickness 0.5mm is shown in the figure 7. The graph shows a maximum transmittance of 77% at 800 nm and it is found to be translucent.

The IR spectrum of the microwave sintered sample in figure 8 shows that it has a maximum transmittance of 72% at 5μm. The good transmittance in the Mid IR range makes it ideal for infrared transparent windows and domes. A slight increase in the infrared cut off is also observed. The improvement in the infrared cutoff is due to the fact that the size of the La\(^{3+}\) ion is slightly greater than the size of the Y\(^{3+}\) ion due to which there is a reduction in vibrational frequency of the system and the absorption edge shifts towards the longer wavelength region according to the relation \( \omega = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} \) where \( \mu = \frac{m_1 m_2}{m_1 + m_2} \) is the reduced mass of the system.

The greater the masses of the atoms the greater the reduced mass and the smaller the vibrational energies \[1\]. The increase in the infrared cut-off along with the enhanced transmittance properties makes La\(_{0.15}\)Y\(_{1.85}\)O\(_3\) a better candidate for infrared transparent window.

4. Conclusions

A single step auto-igniting combustion synthesis is used to prepare nanostructured La\(_{0.15}\)Y\(_{1.85}\)O\(_3\) X-Ray Diffraction (XRD) analysis of the as prepared powder confirms the formation of phase pure cubic La\(_{0.15}\)Y\(_{1.85}\)O\(_3\) nanoparticles. All the peaks in the XRD were indexed to a body centred cubic structure with a calculated lattice parameter \(a=10.632\text{Å}\) 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 \(~16\text{nm}\) 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 La\(_{0.15}\)Y\(_{1.85}\)O\(_3\) is measured in the range 200-800 nm 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 La\(_{0.15}\)Y\(_{1.85}\)O\(_3\) powder is uniaxially compacted in to pellets in a 14mm diameter steel die and sintered to 99% theoretical density without any sintering additives or applying pressure at 1520°C for 20
minitues 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 ~ 430nm. The transmission spectrum of the sintered pellet in the Uv-Vis region reveals that the material is showing 79% of transmittance in the visible region and 72% in the Mid IR region. The presence of La$^{3+}$ ion increases the infrared cut-off. 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 La$_{0.15}$Y$_{1.85}$O$_3$ nanopowder synthesized by the modified auto-igniting combustion technique synthesised using single step combustion method followed by microwave heating can be used very effectively for the fabrication of improved infrared transparent windows and domes.

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