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Influence of La\textsuperscript{3+} ion in the yttria matrix in improving the microhardness of infrared transparent nano La\textsubscript{x}Y\textsubscript{1-x}O\textsubscript{3} sintered via hybrid heating

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Abstract: In the present work, hybrid sintering technique which couples the resistive heating and microwave heating is employed to sinter infrared transparent La\textsubscript{0.15}Y\textsubscript{1.85}O\textsubscript{3} to 99.2% of the theoretical density for the first time to the best of our knowledge. The presence of La\textsuperscript{3+} in the yttria matrix improves the hardness properties to a greater extent without affecting the transmittance properties, but there is a deterioration in the thermal properties of the sample. So we have limited our studies to La\textsubscript{0.15}Y\textsubscript{1.85}O\textsubscript{3} which shows better optical, thermal, and hardness properties. The pellets fabricated from the ultra-fine nano powder with average particle size of ~12 nm synthesized by combustion technique and sintered at 1430 °C with an average grain size of 0.22 µm show ~80.1% transmittance in the UV–visible region and 81% in mid infrared region. For a comparative study of the optical, mechanical, and thermal properties, two other variants of sintering strategies namely conventional sintering and microwave sintering are also employed. A comprehensive analysis on the hardness reveals that the hardness of the pellets sintered via hybrid heating is 9.73 GPa and is superior to the pellets sintered using the other two techniques. The thermal conductivity of the sample is also analyzed in detail. The results clearly indicate that the La\textsubscript{0.15}Y\textsubscript{1.85}O\textsubscript{3} ultra-fine nano powder synthesised by the single-step combustion method and sintered via microwave hybrid heating shows better transmittance properties without compromising the mechanical properties, and can be used very effectively for the fabrication of infrared transparent windows and domes.

Keywords: La\textsuperscript{3+} concentration; microhardness; hybrid sintering; infrared transparent ceramics; thermal conductivity

1 Introduction

Yttria is one of the most extensively studied and promising infrared transparent ceramics due to its excellent properties required for infrared transparent ceramics like isotropic body centred cubic structure which is stable even at 1800 °C [1], moderate refractive index and absence of birefringence [2], high thermal conductivity and low thermal expansion coefficient [3], high thermal shock resistance [4], high melting point [5], low emissivity in the mid infrared range at elevated temperatures [6], and high transparency in the visible and infrared range [7]. But the hardness is at a moderate level compared to other window materials [3,8]. Despite a
reduction in sintering temperature and soaking duration reduces the grain size to a great extent which improves the mechanical and transmittance properties [9].

Sintering of the transparent ceramics to high density without much grain growth is a major challenge in the fabrication of infrared transparent windows. But generally there is a trade-off between the transmittance and mechanical properties. If one looks for improving the transmittance properties, there is a reduction in mechanical properties [10]. As sintering temperature and soaking duration increase, the grain growth gets accelerated which adversely affects the transmittance and mechanical properties. For pure nano yttria, sintering temperature is above 1600 °C. Due to high temperature sintering for long duration, the grains grow in size and the pores trapped within the pellet adversely affect the transmittance properties. A material with larger grain size will have more dislocations piled up, leading to a bigger driving force for dislocations to move from one grain to another. So a relatively less load is required to move from one grain to another. But if the grain size is less, the increased fraction of grain boundaries acts as pinning point which impedes further dislocation propagation, and thereby the hardness increases. La3+ is an effective sintering aid which enhances the transmittance properties of infrared transparent windows [11]. The presence of La3+ ion in the yttria matrix is reported to reduce the sintering temperature to ~1500 °C [12]. La3+ ions enhance the grain boundary mobility of yttria and it is the reason behind improved sinterability [13]. In addition, La3+ ions easily dissolve in the cubic lattice of yttria [14] and reduce the grain growth [15].

Huang et al. [16] utilised a two-step sintering mechanism followed by vacuum sintering to densify La doped yttria to 99.9% of the theoretical density. For this, specimens were first fired in air to 1450 °C without holding then kept at 900 °C for 20 h to attain a density of ~92%. The pellet with minimum porosity was finally sintered at 1700 °C in vacuum to achieve 99.9% density, and the pellet with average grain size of 25 µm and thickness of 1.8 mm showed 77% transmittance at 580 nm. Pellets were isostatically cold pressed at 200 MPa and sintered to 99.7% of the theoretical density at 1700 °C for a soaking duration of 4 h. The sintered pellets with an average grain size of 72 µm showed a transmittance of 73% at 580 nm after an annealing of 20 h at 1300 °C [12]. La2O3 precursors, like La(OH)3 and La2O2CO3, are effectively used to sinter the pellets at 1800 °C to improve the transmittance to 82.72% and 83.34% respectively at 4 µm [11]. Recently Gan et al. [17] used hot pressing sintering to achieve a density of 99.9% in 12 at% La doped yttria ceramics which showed a transmittance of 68.9% at 400 nm and 81.9% at 1100 nm, whereas a pellet sintered without applying pressure achieved 99.8% of the theoretical density. There is not much work reported in this system due to the difficulties in sintering the sample at low temperature with reduced grain size and minimum porosity.

During the missile flight, there is a possibility to have a considerable temperature difference between the outer and the inner surfaces of the window. If the window material is unable to tolerate this thermal stress, it will shatter. Resistance to thermal failure by thermal shock is a critical requirement for some applications. Ideally domes and windows should be made as thin as necessary to withstand aerodynamic pressure to obtain the maximum thermal shock resistance [18]. To achieve high thermal shock resistance figure of merit to prevent the shattering of the window material during the missile flight, it should possess high thermal conductivity. Ideally the thermal conductivity values should be in the range of 7–50 W·m⁻¹·K⁻¹ [19]. Even though the thermal conductivity is playing a vital role in the performance of high quality transparent window, not much work is reported in the literature regarding this.

Due to the increasing need of infrared transparent windows in various applications like infrared windows in homing missiles, transparent armours, infrared inspection ports, infrared cameras, laser technology, lamp envelopes, space craft windows, and modern target acquisition systems, a large amount of research is happening in this field for the last few decades [20–25]. The most recent work is focussing on improving the properties of the currently available materials along with the search of new materials which can be effectively used as infrared transparent windows. In the present work, we discuss in detail the synthesis of LaₓY2₋ₓO₃ by a modified combustion synthesis. The novelty of the present work lies in the sintering strategy adopted by coupling the resistive and microwave heating in a specific proportion. The enhancements in the optical, thermal, and mechanical properties brought
about by the sintering technique are described in detail.

2 Experimental procedure

A single-step auto-igniting combustion technique developed by us was used to synthesize nano structured La$_x$Y$_{2-x}$O$_3$ [26]. Stoichiometric amounts of high purity Y(NO$_3$)$_3$·6H$_2$O and La$_2$O$_3$ (99.99%, Alfa Aesar, USA) were dissolved in double distilled water to make a clear solution. Based on the total valance of the oxidising and reducing agents, the amount of citric acid, which acts as fuel as well as complexing agent, was calculated for maximum release of energy during combustion and was added to the clear solution [27]. 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 $^\circ$C in a ventilated fume hood. The solution boiled on heating and underwent dehydration accompanied by foam. The foam was then ignited by itself on persistent heating giving voluminous and fluffy product of combustion.

The phase purity of the nano powder plays a vital role in the fabrication of the infrared transparent window. The as-prepared samples were characterized by X-ray diffractometer (X’pert pro, PANalytical, the Netherlands) with Cu Kα radiation in the range of 20°–60° in a step of 0.084° for the determination of crystalline structure and phase of the nanomaterials. The average crystallite size was estimated for all the samples from Scherrer’s equation. The phase pure La$_x$Y$_{2-x}$O$_3$ powder was uniaxially compacted into pellets in a 14 mm diameter steel die at 20 MPa using a hydraulic press. The sintering of the disc shaped pellets was carried out in a high temperature furnace with molybdenum heating element (TE-4050, Therelek, India) which employs the resistive heating. Sintering was also carried out using microwave with silicon carbide susceptor (VBCC/MF/86, VB Ceramics Consultants, India) and using a microwave hybrid furnace (VBCC/HMF/71, VB Ceramics Consultants, India). The microwave heating was realized using a pair of 2.45 GHz magnetrons with 1.1 kW each, and for microwave hybrid heating, a pair of molybdenum disilicide heating elements were used in addition to the pair of magnetrons. The experimental density of the sintered pellets was calculated using Archimedes principle. The surface morphological study of the sintered pellets was performed by a scanning electron microscope (NOVA NANOSEM-450, FEI, USA). The transmittance of radiation in the UV–visible and infrared range was measured using UV–Vis (UV-1700, Shimadzu, Japan) and FTIR (Spectrum 2, Perkin-Elmer, Singapore) spectrometers. Thermal conductivity of the samples was measured and compared using nano flash thermal conductivity meter (LFA 447, NETZSCH, Germany). The hardness of the sintered samples was tested using Vickers indenter method (HMV 2TAW, Shimadzu, Japan). Different La$^{3+}$ concentrations were used and analysed in the present work on La$_x$Y$_{2-x}$O$_3$ ($x$ = 0, 0.05, 0.10, 0.15, 0.20, and 0.25). For the ease of discussion, codes were defined as LY1, LY2, LY3, LY4, and LY5 for $x$ = 0.05, 0.10, 0.15, 0.20, and 0.25, respectively. During the course of this work, it was observed that La$_{0.15}$Y$_{1.85}$O$_3$ was the most suited among the pack for window applications. So three variants of sintering namely resistive heating, microwave heating, and hybrid heating were used to densify the sample, and for better understanding, the codes were defined as LY3R, LY3M, and LY3H, respectively, for resistive heating, microwave heating, and hybrid heating.

3 Results and discussion

The phase purity of the crystallites of the as-prepared powder was investigated in detail using X-ray diffraction (XRD) technique. Figure 1 shows the XRD patterns of Y$_2$O$_3$ and La$_x$Y$_{2-x}$O$_3$ ($x$ = 0.05, 0.10, 0.15, 0.20, and 0.25).

All the peaks correspond to the cubic phase of yttria indexed using JCPDS Card No. 895591. No other peaks are observed which clearly indicates that La$^{3+}$ ions are effectually replacing Y$^{3+}$ ions in the yttria cubic

![Fig. 1 XRD patterns of La$_x$Y$_{2-x}$O$_3$ ($x$ = 0, 0.05, 0.10, 0.15, 0.20, and 0.25).](image-url)
structure. But the ionic radius of La$^{3+}$ (1.032 Å) is larger than that of Y$^{3+}$ (0.90 Å) [28], resulting in an increase in $d$ spacing, which is evident from the shift of the diffraction peaks to the lower 2$\theta$ values as indicated by the reference line corresponding to pure yttria in Fig. 1. The shift in peaks towards lower 2$\theta$ values was also reported in the literature in Y$_2$O$_3$/La$_2$O$_3$ system with increase in calcination temperature due to the expansion of Y$_2$O$_3$ lattice along with the lanthanum ion penetration [13,29]. Both materials have 16 formula units per unit cell, allowing calculation of theoretical density [29].

As the concentration of La$^{3+}$ ions increases, the lattice distortion increases and the peaks get broadened due to the lattice strain factor in addition to the size effects. Luo et al. [15] suggested that lattice distortion becomes serious for a composition of $x$ greater than 0.24. In the literature, there are reports that even at elevated temperature of ~1900 °C, the cubic phase is maintained by the yttria system even for 16 mol% addition of La in the yttria matrix [30,31]. The cubic structure of yttria is maintained at least for 12 mol% addition. The phase change for 9 mol% lanthanum doped yttria occurs only after 2325 K [29]. It is found that in the present work, lattice constant changes from 10.613 to 10.658 Å as the La$^{3+}$ concentration changes from 1 to 5 mol%.

To study the sintering behaviour of the sample, different sintering techniques were used, and an effective comparison among the sintering processes which employed resistive, microwave, and microwave hybrid heating was carried out. For effective comparison of the sintering techniques and to optimise the sintering strategy, a number of green pellets with the same pressing conditions were used in the sintering process. After a series of sintering cycles, all the pellets sintered using hybrid heating show high relative density of > 99% of the theoretical density.

The sample LY3 from the group shows enhanced transmittance, infrared cut off, and hardness compared to the pure yttria, and the thermal conductivity is within the range of ideal windows [32]. Further analysis reveals that the samples with higher concentration show very low thermal conductivity which falls below the ideal range and are not desirable for a high quality transparent window which is used for strategic defence and space mission [19]. The variations of thermal conductivity with temperature for different La$^{3+}$ concentration sintered via microwave hybrid heating are shown in Fig. 2.

From Fig. 2, it is clear that the thermal conductivity of the samples decreases drastically with La$^{3+}$ addition. For samples LY4H and LY5H, the thermal conductivity values are very low so that they cannot be used as windows in homing missiles in strategic defence missions. As the La$^{3+}$ ion concentration increases, there may be structural defects introduced into the lattice of yttria. This may reduce mean free path of phonons and thereby enhance phonon scattering which contributes to the reduction in thermal conductivity with La$^{3+}$ concentration [17]. As the best member in the selected composition group, the sintering behaviour of LY3 sample was studied in detail. The relative densities attained by the LY3 sample pellets at different sintering temperatures are shown in Fig. 3.

Initially conventional resistive heating is employed on the sample LY3. It is observed that up to a temperature 1400 °C, the density of the sample
increases sluggishly; but from Fig. 3, it is clear that there is an increase in the sintering rate after 1400 °C. The pellet sintered at 1600 °C for a soaking duration of 2 h achieves a density equal to 98.8% of the theoretical density. This sintering temperature is 20 °C lower than that required for pure yttria reported in our previous work [32]. This high densification without any sintering additives is attributed to the powder quality of the sample produced by modified combustion technique. In microwave sintering, there is no marked difference in densification up to 1300 °C, after which the densification effectively increases and the pellet attains a density of 99% at 1520 °C for a soaking duration of only 20 min. A remarkable reduction in sintering temperature and soaking duration is shown by pellets sintered via hybrid heating. The sintering strategy optimised by us after several trials is utilised in this work as well [32]. That is the resistive heating and microwave heating are effectively coupled in the ratio of 60:40 below 1100 °C and thereafter it is fixed at 40:60. The effectiveness is clearly noticeable in Fig. 3, which is indicated by the early trigger of densification at a comparatively low temperature and the fast densification. In materials like yttria with low dielectric loss, the microwave absorption is negligible at low temperature, but the microwave absorption of the samples increases at high temperature. In microwave sintering, a silicon carbide susceptor is absorbing microwave energy and conventionally transferring to the pellet at low temperature regime. But there is no control over the conventional heating mechanism, whereas in hybrid sintering, the pair of heating elements is used to heat up the sample and we have the control over the resistive heating power as well as the microwave power. The pellets achieve 99.2% of the theoretical density at 1430 °C for a soaking duration of 20 min. A non-linear interaction of microwave with space charges induced by the electric field in a non-perfect crystalline solid generates a force similar to ponderomotive force in plasma science, which may be the reason behind the fast densification of the sample [33].

The densification of the sample with temperature is shown in Fig. 4. The first derivative of the graph shown in Fig. 3 is termed as densification which is equal to

\[
\frac{1}{\rho_0} \left( \frac{d\rho}{dT} \right) \times 100, \quad \text{where} \quad \frac{d\rho}{dT},
\]

density with temperature and \( \rho_0 \) is the theoretical density of the sample. From the figure, it is clear that the densification is almost the same for all up to 1100 °C irrespective of the sintering methods. But for resistive heating, the densification peak around 1520 °C is as expected, whereas the so-called microwave effect is evident in microwave sintering. In microwave sintering, maximum densification is happening at 1440 °C which is ~80 °C lower compared to resistive heating. Hybrid heating employed in this study effectively shifts the maximum densification to lower temperature of 1350 °C by effectively coupling the resistive heating and microwave heating.

The well sintered pellets were hand polished and thermally etched at 1300 °C for 1 h in air in order to study the surface morphology of the sintered samples using scanning electron microscopy (SEM).

Figure 5 shows the SEM micrograph of LY3R sintered to 98.8% of the theoretical density. From the figure, it is evident that the pellet is well sintered with minimum porosity. The grains are distinctly confined
with clear grain boundaries. The image analysis using imageJ and digimizer softwares shows that the grains are in the size range of 0.6–1.8 μm. The grain size distribution curve is shown in the inset, indicating that a majority of grains fall within the size range of 1.0–1.2 μm, and the average grain size of the entire distribution is 1.05 μm.

Figure 6 shows the SEM micrograph of the sintered LY3M pellet. From the micrograph, it is clear that size distribution of the grains is very small compared to that of conventionally sintered pellet. The microwave sintered pellets show 99% of the theoretical density. The grain size distribution curve is shown in the inset. The graph clearly shows that a majority of grains are in the 0.4–0.6 μm range and the average grain size of the entire distribution is 0.43 μm.

SEM micrograph of the LY3H pellet sintered to an optimum sintering density of 99.2% of theoretical density using hybrid furnace is shown in Fig. 7. From the micrograph, it is clear that the pellet is well sintered with minimum pores and the full grown grains are in the size range of 0.1–0.8 μm. The grain size distribution in sintered LY3H pellet is shown in the inset, from which it is evident that a majority of grains lie in the 0.2–0.3 μm range and the average grain size of the entire distribution is as low as 0.22 μm. Hybrid sintering not only densifies the sample, but also restricts any grain growth, resulting the sample with finer microstructure compared to those sintered in resistive heating as well as microwave furnace.

Surface scattering is one of the major barriers which adversely affect the performance of infrared transparent window. In the case of a well sintered sample fabricated from phase pure powder, the scattering contribution from the pores and grain boundaries is negligibly small. So care should be taken in polishing the sample to get mirror quality surface finish. The hand polished pellet was again polished in a self-designed lapping and polishing machine for 1.5–2 h as needed using fine grade diamond paste. The well-polished pellet was used for the transmittance studies. For comparative study, all the pellets were grinded and polished till they attained the same thickness of 0.5 mm. The transmittance of the LY3 pellets sintered via different sintering techniques was analysed and plotted against wavelength and is shown in Fig. 8. A maximum transmittance of 80.1% is shown by the pellet sintered via hybrid heating. The transmittance corresponding to the pellets sintered via resistive heating and microwave heating are 77.2% and 67.4% respectively at 800 nm. The high transmission in hybrid sintered pellet is attributed to the high density, reduced porosity, and reduced grain size.

The transmittance properties of the pellets in the mid infrared range were studied. The upper infrared cut off or the long wavelength edge of transparent ceramics is
determined by the energy absorption used for transition between the vibration state of the lattice called phonons. Usually the overtones of the principal lattice vibration define the upper infrared cut off [34]. Compared to pure yttria sintered via hybrid heating, LY3H is having a slight increase in the transmittance and infrared cut off [32]. The size of La\(^{3+}\) ion is greater than that of Y\(^{3+}\) ion. So the presence of La\(^{3+}\) ion in the yttria matrix changes the vibrational frequency, and as a consequence the upper infrared cut off wavelength slightly shifts to longer wavelength region [2]. So the upper infrared cut off wavelength of La\(^{3+}\) substituted yttria will be more than that of pure yttria. The infrared transmittance spectrum of the pellet sintered using resistive heating in Fig. 9, shows that it has a maximum transmittance of 64\% at 5 μm, whereas the transmittance through the pellet sintered using microwave heating is 72\% at 5 μm. The hybrid sintered pellet shows a maximum transmittance of 81\% in the mid infrared range at 5 μm. In the sample LY3H, the average grain size is very small compared to the samples sintered via the other two sintering methods, and it is found to be less than the wavelength of electromagnetic wave used. If the grain size of the well sintered sample lies below the wavelength of electromagnetic wave used, the scattering contribution from the grain boundary will be negligibly small [9]. The maximum transmittance shown by the sample LY3H is attributed to the reduced grain size in the sintered sample which is a consequence of the absence of secondary phase, hybrid sintering, and the fine quality of the combustion synthesised powder.

Key focus of the present work is the hardness properties of the sample. Improving the hardness of infrared transparent windows without sacrificing the transmittance properties is one of the major challenges in the fabrication of transparent windows [1]. In the present work, to study the effect of load and grain size on the sintered pellets, different loads 0.98, 1.96, 2.94, and 4.9 N were applied on the pellets sintered using resistive heating, microwave heating, and hybrid heating with average grain sizes 1.05, 0.38, and 0.22 μm, respectively. For every load, five indentations were made on the surface at different positions from which the average apparent hardness for a particular load was measured. The hardness values obtained for different loads on the pellets sintered via different techniques are shown in Fig. 10.

The maximum hardness of 10.07 GPa is shown by the pellet sintered via hybrid heating with average grain size 0.22 μm for a load of 0.98 N. Whereas the values are 7.65 and 8.79 GPa respectively for the samples LY3R and LY3M. As indentation load increases, the apparent hardness decreases, i.e., there is a positive indentation size effect (ISE) behaviour. The decrease of hardness with load is minimum in the case of LY3H, whereas the minimum hardness is shown by the pellet LY3R and the decrease in hardness with load is also greater for it. The decrease in hardness with load is maximum for LY3R and is found to be 7.18%. That corresponding to LY3M and LY3H are 4.68% and 1.85%, respectively.

Meyer’s law is generally used to describe the ISE effect by the relation:

\[ P = A \cdot d^n \]

where \( P \) is the load applied, \( d \) is the resultant indent diagonal, and \( A \) and \( n \) are constants. The slope of the graph obtained by plotting \( \ln P \) along \( y \) axis and \( \ln d \) along \( x \) axis is \( n \) and is called as Meyer’s index [35]. To find the Meyer’s index, a graph is plotted with \( \ln P \) along \( y \) axis and \( \ln d \) along \( x \) axis and is shown in Fig. 11. Here
$P$ is the applied load in Newton and $d$ is the diagonal length of indentation in micrometer.

The slopes obtained from the linear fit are 1.91, 1.94, and 1.98 for samples LY3R, LY3M, and LY3H, respectively. All $n$ values are less than 2, which indicate that all the samples show ISE behaviour. For the load independent hardness, the value of $n$ should be 2 [36].

To find the load independent microhardness, proportional specimen resistance (PSR) model [37] is used and compared with modified PSR (MPSR) model [38]. Based on the PSR model, the load $P$ and indentation size $d$ are connected by the relation:

$$\frac{P}{d} = a_1 + a_2 d$$

where $a_1$ is a constant related to the proportional resistance of the specimen which is directly proportional to the Young’s modulus and $a_2$ is a constant related to load independent microhardness $H_0$, and $a_1 / a_2$ is a measure of residual stress connected with the defects in the specimen [37]. A graph $\ln \frac{P}{d}$ versus $d$ is plotted as shown in Fig. 12. The slope $\frac{P}{d}$ is obtained for the samples LY3R, LY3M, and LY3H. The slope of the graph, i.e., $\frac{P}{d^2}$, multiplied by Vickers conversion factor 1.8544 will give the load independent microhardness $H_0$ [39]. The parameters used and the results obtained are tabulated in Table 1. The maximum load independent hardness of 9.73 GPa is obtained for the sample LY3H sintered using hybrid sintering. For the samples LY3M and LY3R, the hardness obtained are 8.06 and 6.67 GPa respectively which are lower compared to that of the sample LY3H.

But in the literature, there are reports that for wide range of loads, some materials show non-linear nature. So a modified PSR (MPSR) model is also used as comparison [40]. It is a semi empirical relation connecting the load $P$ and the indentation size $d$ and is given by

$$P = a_0 + a_1 d + a_2 d^2$$

where $P$ is the applied load, $d$ is the indentation size, $a_0$, $a_1$, and $a_2$ are parameters obtained from curve fitting of the experimental results from Fig. 13. The load independent hardness called true hardness $H_T$ can be obtained from $a_2$ by the relation:

$$H_T = k a_2$$

where $k$ is a constant equal to 1.8544 for Vickers indenter and 14.229 for Knoop indenter [38]. It is reported that the presence of La$^{3+}$ ions in the yttria matrix improves the hardness considerably [15]. So a $P$ versus $d$ graph is plotted for different compositions and the parameters obtained are tabulated in Table 2. The results reveal that as the presence of La$^{3+}$ ions in the matrix increases, the hardness increases, and maximum hardness of 10.05 GPa is shown by the sample LY5H. But due to the adverse effect of La$^{3+}$ ion concentration in the thermal conductivity, we limit our studies to the sample LY3 and is shown in Fig. 14.

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**Table 1** Load independent hardness of LY3 pellets sintered by different fabrication methods based on PSR model

| Sample | $a_1$ (N/µm) | $a_2$ | $H_0$ (GPa) |
|--------|-------------|-------|-------------|
| LY3R   | 0.00818     | 0.00360 | 6.67        |
| LY3M   | 0.00572     | 0.00435 | 8.06        |
| LY3H   | 0.00255     | 0.00525 | 9.73        |

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Fig. 13 Variations in indentation size with applied load for different La concentrations on pellets sintered using microwave hybrid heating.

Table 2 True hardness of $\text{La}_x\text{Y}_{2-x}\text{O}_3$ pellets sintered by different fabrication methods based on MPSR model

| Sample | $a_0$ (N) | $a_1$ (N/µm) | $a_2$ = $\frac{P}{d^2}$ (N/µm$^2$) | $H_t$ (GPa) |
|--------|-----------|--------------|----------------------------------|-------------|
| $\text{Y}_3$ | 0.00064 | 0.00227 | 0.00477 | 8.85 |
| $\text{LY}_{1\text{a}}$ | 0.01011 | 0.00262 | 0.00487 | 9.03 |
| $\text{LY}_{2\text{a}}$ | 0.00690 | 0.00285 | 0.00501 | 9.29 |
| $\text{LY}_{3\text{a}}$ | 0.00182 | 0.00238 | 0.00487 | 9.73 |
| $\text{LY}_{4\text{a}}$ | 0.00520 | 0.00235 | 0.00535 | 9.92 |
| $\text{LY}_{5\text{a}}$ | 0.01638 | 0.00447 | 0.00525 | 10.05 |
| $\text{LY}_{3\text{R}}$ | 0.01398 | 0.00942 | 0.00358 | 6.64 |
| $\text{LY}_{3\text{M}}$ | 0.02014 | 0.00382 | 0.00439 | 8.14 |

Fig. 14 Variations in indentation size with applied load for $\text{LY}_3$ samples sintered via different mechanisms.

The hardness calculated for the sample $\text{LY}_{3\text{H}}$ using PSR model and MPSR model are found to be the same. The grain size of the sintered sample is an important parameter which determines the microhardness. A material with larger grain size will have more dislocation piled up, leading to a bigger driving force for dislocations to move from one grain to another. So a relatively less load is required to move from one grain to another. But if the grain size is less, the increased fraction of grain boundaries acts as pinning points which impedes further dislocation propagation [41]. So the true hardness, i.e., the load independent hardness for the pellet sintered using hybrid sintering is 9.73 GPa, and the greater hardness achieved without compromising the transmittance properties is a remarkable result which may find application in future infrared windows in strategic defence and space missions.

For a better overview of the advantages of the hybrid sintering over microwave and resistive sintering mechanisms, the main results obtained in the present work are tabulated and presented in Table 3. The experimental results clearly indicate that the $\text{LY}_{3\text{H}}$ pellet sintered via hybrid heating is superior to other pellets sintered via resistive heating and microwave heating. The high transmittance of 80.1% in the UV–visible and 81% in the mid infrared region without compromising the thermal and mechanical properties is remarkable results which will open doors for this novel sintering mechanism to many fields of materials science especially the branch of ceramic processing.

Table 3 Comparison of results obtained from pellets sintered via resistive heating, microwave heating, and hybrid heating

| Sample | $\text{LY}_{3\text{a}}$ | $\text{LY}_{3\text{R}}$ | $\text{LY}_{3\text{M}}$ |
|--------|----------------|----------------|----------------|
| Sintering temperature (°C) | 1590 | 1520 | 1430 |
| Heating rate (°C·min$^{-1}$) | 10 | 40 | 40 |
| Soaking duration (min) | 120 | 20 | 20 |
| Density (%) | 98.8 | 99.0 | 99.2 |
| Average grain size (µm) | 1.05 | 0.43 | 0.22 |
| Transmittance in UV–visible region at 800 nm (%) | 67.4 | 77.2 | 80.1 |
| Transmittance in mid infrared region at 4 µm (%) | 64 | 72 | 81 |
| Infrared cut off wavelength (µm) | 9.4 | 9.4 | 9.5 |
| Thermal conductivity at 300 K (W·m$^{-1}$·K$^{-1}$) | 11.81 | 11.27 | 11.01 |
| Load independent hardness (GPa) | 6.64 | 8.14 | 9.73 |

4 Conclusions

Nanostructured $\text{La}_x\text{Y}_{2-x}\text{O}_3$ ($x = 0, 0.05, 0.10, 0.15, 0.20,$ and $0.25$) powder is synthesised by a single-step auto-igniting combustion technique. As a better candidate, we have selected $\text{LY}_3$ and it has an average particle size of 12 nm. XRD results are indexed with JCPODS Card No. 895591 reference of pure cubic yttria which shows that $\text{La}^{3+}$ ions clearly dissolve in yttria
matrix. The variation in the peak position with different compositions is clearly observable in the XRD pattern which is attributed to the increased ionic radius of La\(^{3+}\) ion compared to Y\(^{3+}\). The prime novelty of this work is that we are able to develop a new sintering schedule to couple resistive and microwave heating to sinter the samples to high density (> 99%) without any sintering aids or pressure. In this hybrid sintering, there is a substantial reduction in sintering temperature and soaking duration. The pellet sintered via hybrid heating shows reduced grain size, minimum porosity, improved transmittance in the UV–visible and mid infrared range, and better hardness compared to the microwave sintered and resistive sintered counterparts. Among different samples with different compositions, the sample LY3 which contains 3 mol% La\(^{3+}\) is selected as a better candidate, because as La\(^{3+}\) ion concentration increases, the thermal conductivity is affected adversely. By resistive heating, disc shaped pellets made from the sample LY3 are sintered to 98.8% of the theoretical density at 1590 °C for 2 h without any sintering additives or applying pressure. The average grain size obtained is 1.05 μm and a well-polished pellet shows a transmittance of 67.4% in the visible region and 64% in the mid infrared region. In microwave sintering, pellets sintered to 99% of the density at 1520 °C for a soaking duration of 20 min with average grain size of 0.43 μm show 77.2% transmittance in the UV–visible region and 72% in the mid infrared region. But through microwave hybrid heating, the pellets achieve a density 99.2%, a substantial reduction in sintering temperature to 1430 °C and soaking time of 20 min of the sample is observed with reduced average grain size of ~0.22 μm and the pellet showed enhanced transmittance of 80.1% in the visible and 81% in the mid infrared region. There is a nominal reduction in the thermal conductivity and diffusivity of the pellet sintered using hybrid heating compared to the other two pellets but the values are in the ideal range suitable for infrared transparent windows. The pellet sintered using hybrid heating shows high load independent hardness of 9.73 GPa and is a remarkable result that it is achieved without compromising the transmittance properties. The hardness corresponding to the pellets sintered using microwave and resistive heating are 8.14 and 6.64 GPa respectively. It is observed that as La\(^{3+}\) ion concentration increases, the hardness and infrared cut off increases but the thermal conductivity decreases. The microwave hybrid sinterability also increases with La\(^{3+}\) concentration. The results clearly indicate that the yttria powder with La\(^{3+}\) ions in the lattice synthesised using single-step combustion method followed by microwave hybrid sintering can be used very effectively for the fabrication of improved infrared transparent windows and domes.

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