Available online at www.sciencedirect.com

SciVerse ScienceDirect

Ceramics International 38 (2012) 4131–4135

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

Novel amorphous precursor densification to transparent Nd:Y_2O_3 Ceramics

Rekha Mann *, Kiranmala Laishram, Sheikh Ashfaq Ahmed, Neelam Malhan

Laser Materials Division, Laser Science and Technology Centre, DRDO, Metcalfe House, Delhi 110054, India

Received 16 November 2011; received in revised form 27 January 2012; accepted 27 January 2012
Available online 4 February 2012

Abstract

A novel approach of neodymium ion doped yttrium oxide (Nd:Y_2O_3) amorphous precursor compaction and sintering is being reported for the first time. Precursor of 2 at.% Nd^{3+} doped Y_2O_3 was synthesized by gelation of sol of yttrium and neodymium nitrates with L-alanine at 80 °C for 16 h followed by gel combustion in microwave. A part of microwave precursor was heat treated at 700 °C for 5 h to give the partially crystalline Nd:Y_2O_3 amorphous precursor. Thermogravimetric analysis (TGA) of partially crystalline amorphous precursor of Nd:Y_2O_3 gave 8.5% total weight loss indicating removal of maximum organics. X-Ray diffraction (XRD) showed broad peaks indicating incomplete crystallization of cubic Nd:Y_2O_3. Morphology was found to be close to spherical with particles in size range 17–19 nm by TEM. Another part of microwave precursor on calcination at 1000 °C for 3 h led to formation of fully crystalline Nd:Y_2O_3 with particles in size range of 35–85 nm. Both partially crystalline amorphous precursor and fully crystalline Nd:Y_2O_3 were compacted at 400 MPa by cold isostatic press and sintered at 1750 °C for 10 h under vacuum (10^{-5} mbar). The partially crystalline Nd:Y_2O_3 amorphous precursor densified to 99% with 65% transmission at 2500 nm (0.5 mm thickness) compared to 96% densification with 34% transmission for fully crystalline Nd:Y_2O_3 without any sintering aids. Retention of cubic phase purity of Y_2O_3 was observed in both the ceramic pellets post sintering by XRD. Good grain fusion with grain growth to ≤ 2 μm was observed by scanning electron microscope (SEM) for partially crystalline Nd:Y_2O_3 amorphous precursor. Thus partially crystalline Nd:Y_2O_3 amorphous precursor nanopowders, with homogeneous close to spherical fine particles and high reactivity due to ionic mobility of amorphous phase, led to better densification.

Keywords: Nd:Yttria; Microwave gel combustion; Precursor sintering; Transparent ceramic

1. Introduction

Cubic yttria (Y_2O_3) has high thermal stability, corrosion resistivity and transparency over a wide wavelength region thus making it useful as a laser host material [1,2]. It is extremely difficult to grow large-size high quality Y_2O_3 single crystal by conventional growth methods because of very high melting temperature (2430 °C) of Y_2O_3 and structural phase transition at 2280 °C [3]. Thus for laser applications it can be fabricated only in the form of ceramics by powder technology [4]. Typically to obtain transparent yttria ceramics, nanopowder compacts are sintered at 2000 °C under normal pressure for long periods. Yttria nanopowder compacts can also be sintered under high pressure at 1500 °C with addition of some sintering aids, such as ThO_2 [5], La_2O_3 [6], HfO_2 and LiF [7]. However, these sintering aids have a significant influence on the physical and chemical properties of the final product. Therefore, it is of great importance to synthesize ultrafine, low-agglomerated and spherical yttria nanopowders with high sinterability and reactivity leading to formation of dense transparent ceramics [8] without sintering aids.

In the present work novel approach of partly crystalline Nd:Y_2O_3 amorphous precursor sintering and densification is being followed for the first time. Comparison of sintering and densification with calcined, fully crystallized Nd:Y_2O_3 nanopowder is being explored.

2. Experimental procedure

Yttrium nitrate, $Y(NO_3)_3 \cdot 6H_2O$ (99.9% purity Alfa Aesar), neodymium nitrate, $Nd(NO_3)_3 \cdot 6H_2O$ (99.9% purity Alfa Aesar) and L-alanine ($\geq$99.5% purity Fluka) were used as the starting materials. The metal nitrates were taken in the molar ratios of $Y_{2.94}Nd_{0.06}$. L-alanine was used as the complexing agent as well

---

* Corresponding author. Tel.: +91 11 23907513; fax: +91 11 23811319.
E-mail address: mann_rekha@lastec.drdo.in (R. Mann).

0272-8842/$36.00 © 2012 Elsevier Ltd and Techna Group S.r.l. All rights reserved.
doi:10.1016/j.ceramint.2012.01.072

as fuel keeping amino acid to metal nitrate (A/N) ratio of 0.5:1. The sol was prepared in high purity water of resistivity >5 MΩ cm. Gelation took place at 80 °C for 16 h. Drying of the gel was carried out in domestic microwave oven modified for exhaust gases. The gel underwent rapid blast giving fluffy powder within 10 min to give precursor. A part of microwave precursor was treated at 700 °C for 5 h to evolve the organic content to give partially crystalline Nd:Y_2O_3 amorphous precursor. Other part of microwave precursor was calcined at 1000 °C for 3 h to give fully crystalline cubic Nd:Y_2O_3 nanopowder. Phase identification of powders were performed using Philips X-ray diffractometer, PW 3020 in 2θ range from 15 to 80° keeping step size 0.02. Crystallite size was calculated using Scherrer's equation [9]

$$t = \frac{0.9\lambda}{(\beta_{sample}^2 - \beta_{inst}^2)^{1/2}\cos\theta}$$

where t is the crystallite diameter, $\lambda = 1.54056$ Å, θ is the diffraction angle, β_{sample} is the full width at half maximum (FWHM) of the diffraction peak and β_{inst} is characteristic of the instrument. Fourier transform infrared spectra (FTIR) of powders were recorded on FTIR Spectrometer (Bruker, model Vector 22) using KBr pellets. Morphology and size range of the nanopowders were observed using transmission electron microscope (TEM, FEI Philips Morgagni 268D, AC voltage 100 kV and magnification up to 280,000×).

Thermogravimetric analysis (TGA) of microwave combusted powder was carried out in air at the heating rate of 10 °C/min from room temperature to 900 °C, on Perkin Elmer Diamond Simultaneous TGA/DTA.

Partially crystalline amorphous precursor and fully crystalline Nd:Y_2O_3 nanopowders were milled separately and each was uniaxially pressed in a 13 mm diameter steel die lined with tungsten carbide at 34 MPa. The compacts were then pressed isostatically at 400 MPa. The green compacts were sintered at 1750 °C for 10 h under vacuum in a furnace with tungsten and molybdenum mesh heaters, heating and cooling rates were 600 °C/h. Vacuum in furnace was better than 1×10^{-3} Pa. Densities of the pellets were obtained using Archimedes principle taking theoretical density of Y_2O_3 to be 5.031 g/cm^3.

The sintered specimen was analyzed for retention of phase purity by XRD and specimen was polished and gold coated to observe microstructure using scanning electron microscope (LEO-1430). Transmission of sintered and polished samples was done by Cary 5000 UV–VIS–NIR spectrophotometer.

3. Results and discussion

From TGA (Fig. 1a) it was seen that microwave combusted Nd:Y_2O_3 precursor showed ~15% weight loss up to 200 °C due to absorbed moisture, while residual nitrates were lost between 200 and 550 °C with weight loss of ~19%. From 550 to 700 °C weight loss of only 2.5% was observed. No major weight loss was observed after 700 °C. Thus total weight loss of ~37% was observed upto 900 °C. So Nd:Y_2O_3 microwave precursor was heat treated at 700 °C for 5 h to burn out organics. TGA (Fig. 1b) of precursor heat treated at 700 °C for 5 h showed ~8.5% total weight loss indicating that maximum organics have been burnt out. Heat treatment at 700 °C for 5 h was done to retain amorphous phase of Nd:Y_2O_3 along with partial crystalline phase, supported by XRD discussed below.

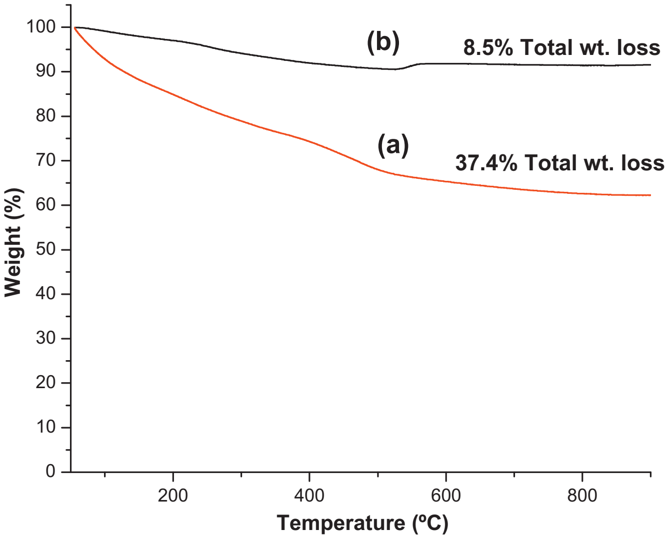

Fig. 1. TGA of Nd:Y_2O_3 (a) microwave precursor and (b) microwave precursor heat treated at 700 °C for 5 h.

FTIR of microwave combusted precursor of Nd:Y_2O_3 (Fig. 2a) on calcination at 1000 °C for 3 h showed group of peaks at 559, 465, 419 cm^{-1} quite consistent with metal oxygen bond in Y_2O_3 [10,11]. Nd:Y_2O_3 microwave precursor treated at 700 °C for 5 h showed (Fig. 2b) incompletely formed small peaks at 559 and 419 cm^{-1}. So further investigation is required to be done by XRD, for single phase cubic yttria formation.

XRD (Fig. 3a) of microwave combusted Nd:Y_2O_3 precursor treated at 700 °C for 5 h, though showed major broad peaks characteristic of cubic yttria in accordance with JCPDS 88-2168, but complete crystallization is not seen. This indicated

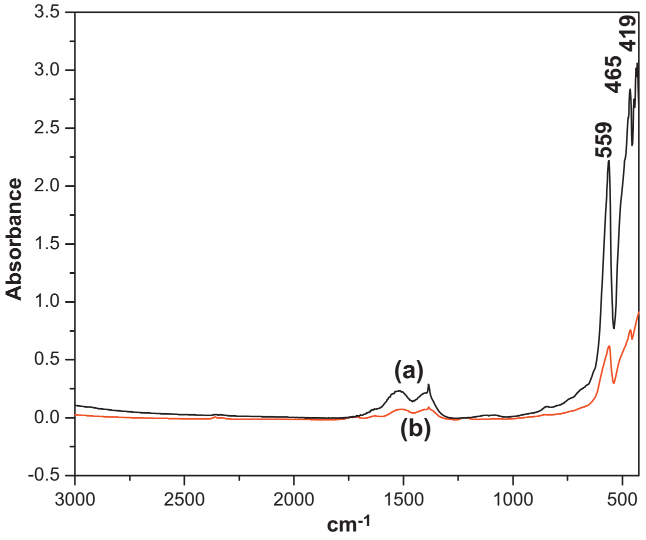

Fig. 2. FTIR of Nd:Y_2O_3 microwave precursor (a) calcined at 1000 °C for 3 h and (b) heat treated at 700 °C for 5 h.

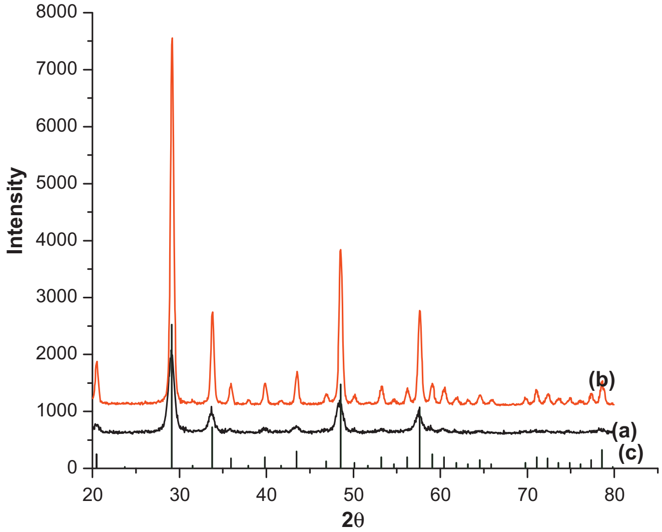

Fig. 3. XRD of Nd:Y_2O_3 microwave precursor (a) heat treated at 700 °C for 5 h, (b) calcined at 1000 °C for 3 h and (c) JCPDS 88-2168.

partial crystallization of cubic yttria phase, which was supported by electron diffraction pattern by TEM. XRD (Fig. 3b) of microwave combusted Nd:Y_2O_3 precursor on calcination at 1000 °C for 3 h, showed sharp well defined peaks of fully crystalline cubic Nd:Y_2O_3 nanopowder. For partly crystalline Nd:Y_2O_3 amorphous precursor the primary particle size was calculated to be 17 nm, by taking the FWHM value of broad peaks in Scherer's equation. The primary particle size was calculated to be 30 nm for fully crystalline cubic Nd:Y_2O_3 nanopowder.

Partially crystalline Nd:Y_2O_3 amorphous precursor obtained after heat treatment at 700 °C for 5 h, showed uniform and close to spherical morphology with fine particles in the size range of 17–19 nm by TEM (Fig. 4a). Small particle size speed up material transport leading to rapid densification [12] and spherical morphology is highly sinterable [2]. Thus partially crystalline Nd:Y_2O_3 amorphous precursor powders are expected to undergo fast densification during sintering. Electron diffraction pattern of partially crystalline Nd:Y_2O_3 amorphous precursor (Fig. 4b) showed amorphous halo confirming incomplete crystallization. Nd:Y_2O_3 microwave precursor on calcinations at 1000 °C for 3 h resulted in complete crystallization of cubic yttria, observed by crystalline ring pattern in electron diffraction pattern (Fig. 5b), with close to spherical particle of size range 30–75 nm by TEM (Fig. 5a). Thus calcination at 1000 °C for 3 h resulted in large particle size.

Partially crystalline amorphous precursor and fully crystalline Nd:Y_2O_3 nanopowders compacts on sintering at 1750 °C for 10 h under 1.3×10^{-3} Pa gave ceramics, which showed transmissions of 65% and 32.5% respectively at 2500 nm (Fig. 7). For Y_2O_3 the refractive index is equal to 1.74 which leads to Fresnel losses of 14% [13]. Both the samples were uncoated and Fresnel losses of 14% were not accounted. Both the sintered samples revealed characteristics Nd^{+3} absorption lines in the visible and near-IR spectral range [13,14].

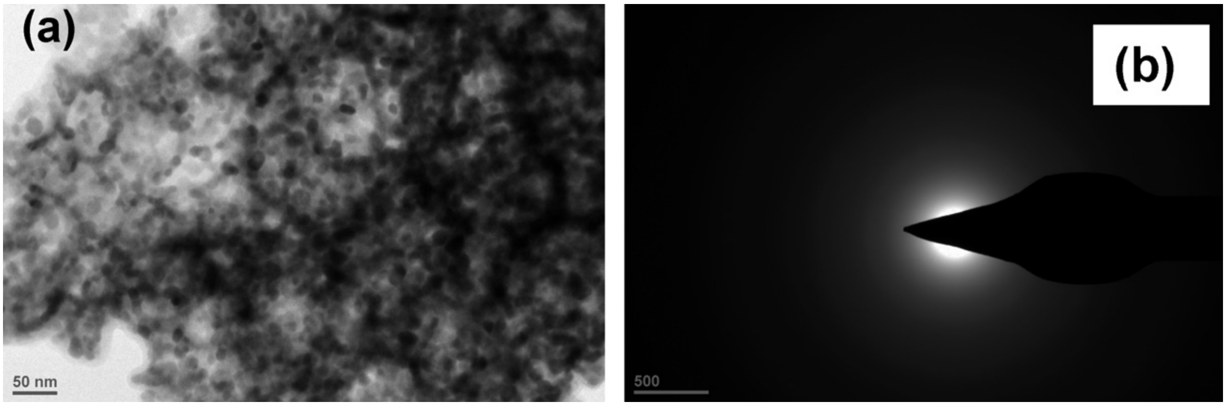

Fig. 4. (a) TEM of Nd:Y_2O_3 microwave precursor heat treated at 700 °C for 5 h and (b) electron diffraction pattern.

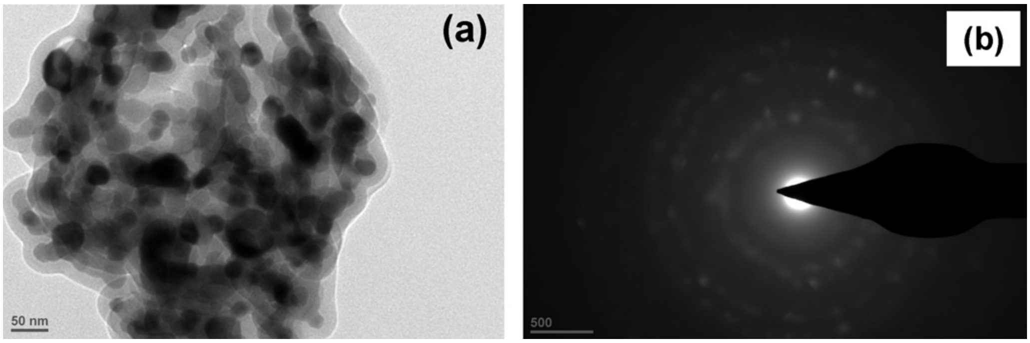

Fig. 5. (a) TEM of Nd:Y_2O_3 microwave precursor calcined at 1000 °C for 3 h and (b) electron diffraction pattern.

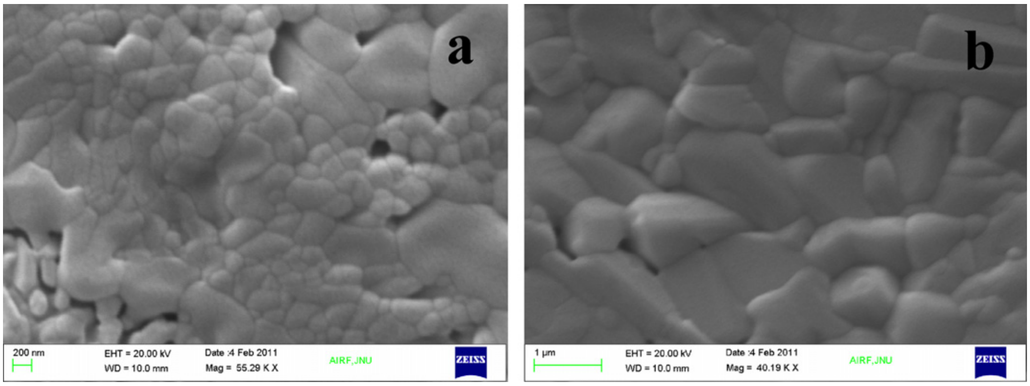

Fig. 6. SEM of sintered ceramic derived from Nd:Y_2O_3 microwave precursor (a) heat treated at 700 °C for 5 h and (b) calcined at 1000 °C for 3 h.

SEM (Fig. 6) of polished, etched and gold coated surface of sintered pellets, derived from partially crystalline Nd:Y_2O_3 amorphous precursor nanopowders, showed maximum grain fusion with grain growth upto $\leq 2\ \mu m$ leading to 99% densification with 65% transmission (Fig. 7a). For sintered pellets derived from fully crystalline Nd:Y_2O_3 nanopowders incomplete grain fusion with a lot of residual porosity led to reduction in densification to 96% and transmission upto 32% (Fig. 7b).The higher sinterability of the partly crystalline amorphous powder is due to open structure of amorphous phase resulting in higher ionic mobilities, as observed in case of consolidation of amorphous powder to dense ytrrium aluminium garnet nanoceramics [15]. Further partly crystalline Nd:Y_2O_3 amorphous precursor nanopowders are narrow in size range with maximum particles with size ~17 nm, with close to spherical shape and soft agglomeration. These soft agglomerates are highly compressible, because the weak attractive forces between soft agglomerates can be broken down easily to smaller primary particles by mechanical force, resulting in fast densification and rapid sintering [16]. Due to practical difficulty of undesirable grain growth during sintering, partly crystalline Nd:Y_2O_3 amorphous precursor nanopowder densification provide a option for densification without major grain growth [17]. On the other hand fully crystalline Nd:Y_2O_3 nanopowders have wide size range of 30–85 nm and hard agglomeration due to high temperature calcinations, which result in differential sintering leading to formation of residual porosity and subsequent lesser densification.

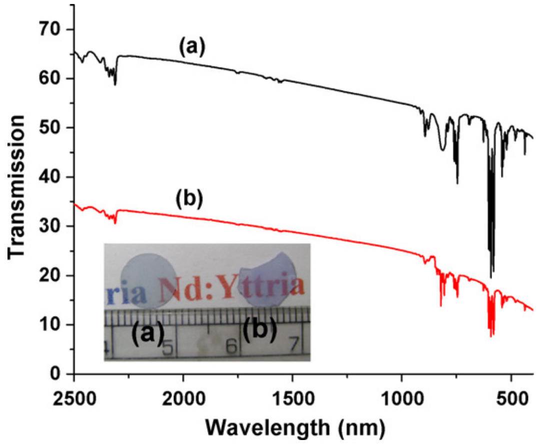

Fig. 7. Transmission of sintered ceramic derived from Nd:Y_2O_3 microwave precursor (a) heat treated at 700 °C for 5 h and (b) calcined at 1000 °C for 3 h.

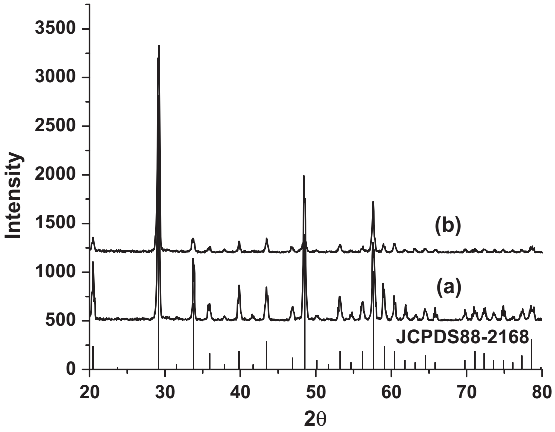

Fig. 8. XRD of sintered ceramic derived from Nd:Y_2O_3 microwave precursor (a) heat treated at 700 °C for 5 h and (b) calcined at 1000 °C for 3 h.

XRD of sintered pellets showed phase purity for both the types of Nd:Y_2O_3 nanopowders (Fig. 8), indicating complete crystallization during reactive sintering of partially crystalline Nd:Y_2O_3 amorphous precursor.

4. Conclusions

A novel route of partially crystalline Nd:Y_2O_3 amorphous phase densification and reactive sintering to transparent Nd:Y_2O_3 ceramic is described for the first time. Microwave precursor obtained by nitrate alanine microwave gel combustion method were heat treated at 700 °C for 5 h, to give highly reactive nanopowders with incomplete yttria phase formation, but with spherical shape and size ~17 nm. Sintered ceramic from this powder gave 65% transmission with 99% densification with in situ phase pure yttria formation during sintering.

References

[1] T. Ikegami, J.G. Li, M. Toshiyuki, Fabrication of transparent yttria ceramics by the low-temperature synthesis of yttrium hydroxide, J. Am. Ceram. Soc. 85 (7) (2002) 1725–1729.

[2] A. Dupont, A. Largeteau, C. Parent, G.B. Le, H. Jean-Marc, Influence of yttria powder morphology on its densification ability, J. Euro. Ceram. Soc. 25 (2005) 2097–2103.

[3] A. Ikesue, K. Kamata, K. Yoshida, Synthesis of transparent Nd-doped HfO_2–Y_2O_3 ceramics using HIP, J. Am. Ceram. Soc. 79 (2) (1996) 359–364.

[4] H. Zhenguo, S. Xudong, X. Zhimeng, C. Shaowei, T. Chi-Tay, Precipitation synthesis and sintering of yttria nanopowders, Mater. Lett. 58 (2004) 2137–2142.

[5] C. Greskovich, K.N. Woods, Fabrication of transparent ThO_2-doped Y_2O_3, Am. Ceram. Soc. Bull. 52 (1973) 473–478.

[6] Q.H. Yang, J. Xu, L.B. Su, H.W. Zhang, Spectroscopic characteristics of transparent. Yb:$Y_{2-2x}La_{2x}O_3$ laser ceramics, Acta Phys. Sin. 55 (2006) 1207–1210.

[7] R.A. Lefever, J. Matsko, Transparent yttrium oxide ceramics, Mater. Res. Bull. 2 (9) (1967) 865–869.

[8] R.V. Mangalaraja, J. Mouzon, P. Hedstrom, I. Kero, K.V.S. Ramam, C.P. Camurri, M. Oden, Combustion synthesis of Y_2O_3 and Yb–Y_2O_3 Part I. Nanopowders and their characterization, J. Mater. Proc. Technol. 208 (1-3) (2008) 415–422.

[9] B.D. Culity, S.R. Stock, Elements of X-Ray Diffraction, second ed., Addition-Wesley, MA, 1978.

[10] T.K. Vishnuvardhan, V.R. Kulkarni, C. Basavaraja, S.C. Raghavendra, Synthesis, characterization and ac conductivity of polypyrrole/Y_2O_3 composites, Bull. Mater. Sci. 29 (1) (2006) 77–83.

[11] L.D. da Vila, E.B. Stucchi, M.R. Davolos, Preparation and characterization of uniform, spherical particles of Y_2O_2S and Y_2O_2S:Eu, J. Mater. Chem. 7 (10) (1997) 2113–2116.

[12] J. Mouzon, P. Nordell, A. Thomas, M. Odén, Comparison of two different precipitation routes leading to Yb doped Y_2O_3 nano-particles, J. Eur. Ceram. Soc. 27 (4) (2007) 1991–1998.

[13] H. Zhou, Q. Yang, J. Xu, H. Zhang, Preparation and spectroscopic properties of 2% Nd:$(Y_{0.9}La_{0.1})_2O_3$ transparent ceramics, J. Alloys Compd. 471 (1-2) (2009) 474–476.

[14] N.S. Prasad, W.C. Edwards, S.B. Trivedi, S.W. Kutcher, C.C. Wang, J-S Kim, Recent progress in the development of neodymium-doped ceramic yttria, IEEE J. Selected Topics Quant. Electron. 13 (3) (2008) 831–837.

[15] S. Choudhury, A.S. Gandhi, V. Jayaram, Bulk, dense, nanocrystalline yttrium aluminum garnet by consolidation of amorphous powders at low temperatures and high pressures, J. Am. Ceram. Soc. 86 (2) (2003) 247–251.

[16] M.N. Rahaman, Ceramic Processing and Sintering, Marcel Dekker, Inc., USA, 1995.

[17] L. Mei, G. He, L.L. Wang, G.H. Liu, J.T. Li, Fabrication of transparent $LaAlO_3$/t-ZrO_2 nanoceramics through controlled amorphous crystallization, J. Eur. Ceram. Soc. 31 (9) (2011) 1603–1609.