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Journal of the European Ceramic Society 27 (2007) 1165–1169
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Fabrication of Nd:Y_2O_3 transparent ceramics by pulsed compaction and sintering of weakly agglomerated nanopowders

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Abstract

In this paper the fabrication of dense, optically transparent ceramics by compaction and sintering of nanosized Y_2O_3 powders, doped by different Nd_2O_3 content (1.0 and 3.3 mol%) is investigated. The sintering temperature was decreased substantially, and there were no extra additives inserted into basic oxide due to high nanosystem activity. The as synthesized powder was transformed from monoclinic to cubic modification by the preliminary calcination in air at 800 °C in order to avoid cracking during sintering. This phase transformation of the starting powder, annealing of the compacts in air (1200 °C) and sintering in vacuum for 1 h at 1700 °C allowed to fabricate optically transparent ceramics with well-formed boundaries, average crystalline size of 30–40 μm and vanishingly small porosity with pore size less than 0.5 μm.

Keywords: Calcination; Pressing; Sintering; Porosity; Glass ceramics

1. Introduction

Much attention is paid recently to the development of optically transparent polycrystalline materials due to their fine thermal–mechanical properties and the possibility of doping with rare earth ions. In terms of laser physics, a ceramic material compared to a single crystal has several advantages, namely: ease of fabrication, less expensive, fabrication of large size and high additive concentration, multi-layer and multi-functional ceramic structure, mass production, etc.[1,2] Optically transparent Y_2O_3 appears to be a perspective laser material, because its thermal conductivity is 2 and 10 times higher than thermal conductivity of YAG and glass, correspondingly.[3] This allows obtaining essentially higher powers of laser radiation, generated on Nd^{3+} ion. Although due to its high melting temperature, ∼2400 °C and high technological requirements,[2,4] this material is used rarely, that is why its fabrication is not enough investigated.

Certain "packing" additives (e.g. hafnium, thorium and zirconium oxides[5–9]) are almost always used when fabricating the transparent materials by solid-phase sintering. In this case some conditions for complete pore elimination are created. The additives that form a solid solution with the basic oxide are of the most interest, because it results in highest density and transparency of the ceramics in terms of monophase maintenance.[10]

In order to fabricate full dense ceramics one has to create certain conditions of pore elimination, moreover this process has to run against slow crystalline growth. In known works[5–9] it was provided by the introduction of certain additives into the material and also by temperature (1900–2150 °C) and gas regimes of sintering.

In present paper the fabrication of dense, optically transparent ceramics by solid-phase sintering of nanosized Y_2O_3 powders, doped by different Nd_2O_3 content is investigated. High activity of such nanosystem allows to avoid the insertion of any "packing" additives and to decrease substantially the temperature of sintering.

2. Experiment

The nanopowders of Nd:Y_2O_3 solid solutions with different mole content of neodymium (1.0% and 3.3%) were synthesized by target evaporation with a pulse-periodic CO_2 laser.[11] The targets were fabricated from microsized Y_2O_3 and Nd_2O_3 powder mixtures. The average laser power of 500–600 W led up to 25 g/h

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doi:10.1016/j.jeurceramsoc.2006.05.027

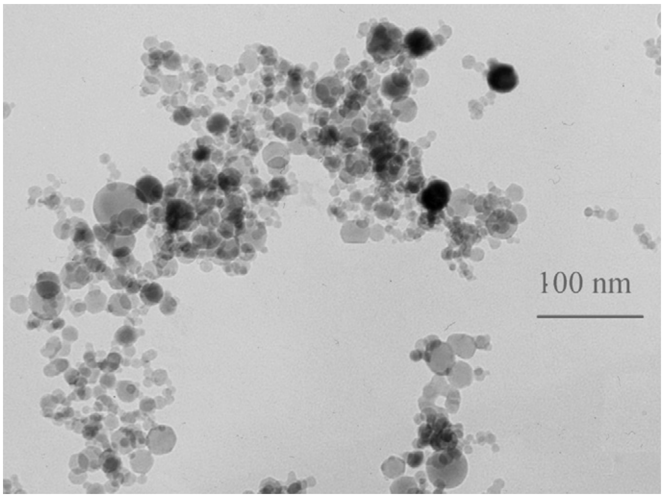

Fig. 1. TEM micrograph of 1.0Nd:Y_2O_3 starting nanopowder.

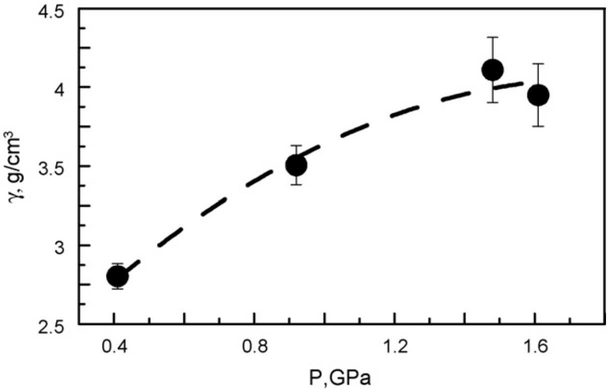

Fig. 2. The dependence of 3.3Nd:Y_2O_3 compacts density from the amplitude of applied pulsed pressure.

nanopowder output. After laser synthesis the powders were sedimented in isopropyl alcohol in order to eliminate fractions that were larger than 200 nm. Weak agglomeration of the particles after drying was the most important quality of the powder; the agglomerates of nanoparticles were easily broken by the ultrasonic treatment when placed again in the alcohol (Fig. 1). It was clearly seen in the SEM micrographs (JEM-200) that the particle images were mainly circle-shaped, hence one can assume that the particles were spheres.

Obtained powders were certified regarding to X-ray diffraction composition (modification and lattice parameter), specific surface area (S_{BET}), average crystalline size (d_x), mass ($\Delta M/M$) and volume ($\Delta V/V$) content of adsorbats upon heating up to 450 °C (Table 1). It is worth mentioning that X-ray diffraction analysis (in filtered Cu K_α-radiation with DRON-4M tool) revealed that the obtained powder compounds were single-phase solid solutions in metastable monoclinic modification.

The nanopowders, previously degassed in the vacuum chamber, were pressed into pellets (disks) with the diameter of 15 and 32 mm and 0.5–1.5 mm thick with the uniaxial magnetic-pulsed press.[12,13] The amplitude of the applied pressure was up to 1.6 GPa. After compaction the green bodies were exposed to heat in order to decrease the internal stresses. During the experiment the degassing and stress relieving temperatures were varied in a wide range from 20 to 450 °C.

The compaction and sintering of the starting powder as well as the powder, transformed to cubic modification by preliminary calcination were investigated. A set of green bodies was annealed in air for 1 h at 1200 °C, and then the samples were sintered in the vacuum furnace ($\sim 10^{-3}$ Pa) at temperatures of up to 1700 °C. The sintering kinetics was also investigated with dilatometer (NETZSCH DIL 402 C) in vacuum at 1525 °C in two heating modes: constant heating rate (CHR) and constant sintering rate also known as rate control sintering mode (RCS). The shrinkage of the samples and porosity of the final ceramics were measured. The sintered samples were analyzed by AFM (Solver 47p), SEM (LEO 982) and X-ray diffraction.

3. Results and discussion

Applying of pulsed pressures at room temperature to the as synthesized powder in monoclinic modification resulted in fabrication of uniform, crackless compacts with the densities of up to 4.12 g/cm^3 (Fig. 2), which corresponds to 83% of relative density. Unfortunately the following sintering led to their partial or complete destruction. This effect can be explained in two ways: the extraction of large amount of adsorbats from the compacts (see $\Delta V/V$ in Table 1) and the contraction of the sintered sample volume approximately by 0.4–0.5% during the transformation from monoclinic to cubic phase.

Despite the bulk extraction of the adsorbats, the thermal treatment before and after the compaction did not bring any essential density changes, moreover the compacts, which were obtained in this mode remained unified. But it did not solve the cracking problem during sintering, indicating that the main destruction mechanism was the phase transformation and the role of water absorbency was not significant.

Probably, the occurrence of cracks during sintering can be explained by the bulk shrinkage anisotropy of the green body upon phase transformation from monoclinic to cubic modification.

As a result it was suggested to transform the as synthesized powder from monoclinic to cubic phase before shaping with

Table 1
The main characteristics of Nd:Y_2O_3 starting powders

Powder type	Nd (mol%)	S_{BET} (m^2/g)	d_x (nm)	450 °C		Lattice type	Lattice parameter			
				$\Delta M/M$ (%)	$\Delta V/V$ (%)		a (Å)	b (Å)	c (Å)	β (°)
1.0Nd:Y_2O_3	1.0	60	17	9.35	34.2	Monoclinic	13.922	3.490	8.615	99.93
3.3Nd:Y_2O_3	3.3	73	15	7.07	26.1	Monoclinic	14.690	3.496	9.066	110.50

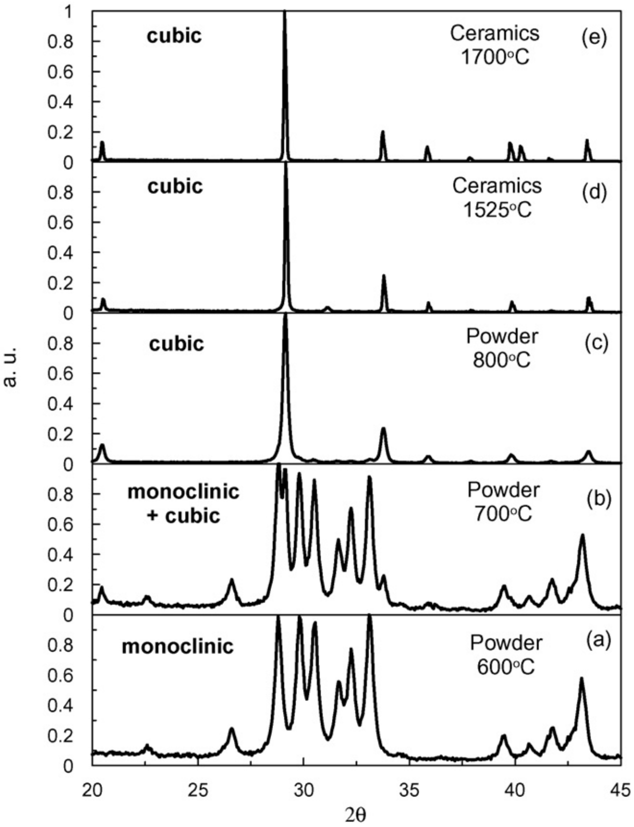

Fig. 3. X-ray diffraction pattern of 1.0Nd:Y_2O_3 starting powders, calcined at (a) 600 °C, (b) 700 °C, (c) 800 °C, ceramics, sintered at (d) 1525 °C and 3.3Nd:Y_2O_3 ceramics, sintered at (e) 1700 °C.

pulsed pressure. That is why a set of powders, calcined in air for 1 h at different temperatures, namely 600, 700, 800, 900, 1000, 1100 °C was prepared in order to determine the phase transformation conditions. X-ray diffraction investigation showed (Fig. 3a–c) that the starting powder was transformed partially from monoclinic to cubic phase after 700 °C calcination and almost completely at 800 °C (Fig. 3c).

Fig. 4 shows the dependences of average crystalline size, d_x, specific surface area, S_{BET}, and cubic phase content in Nd:Y_2O_3 from the calcination temperature of the starting powder. Here the symbols correspond to experimental data and the lines are their splined approximations.

X-ray diffraction analysis showed that the increase of the powder calcination temperature increases its crystalline growth and decreases its specific surface area. It should be pointed out that the character of d_x and S_{BET} curves is changed around 600–800 °C. It is evidently explained by the reforming of the oxide crystalline lattice, which occurs during the phase transformation in the given temperature range (Fig. 4c).

It should be mentioned that the increase of the calcination time of the powders at 600 and 700 °C by 10 times increased the crystalline size by 0.6% in the first case and by 0.7% (monoclinic modification) and 4% (cubic modification) in the second case, moreover the cubic phase content in the oxide after 700 °C treatment increased from 35% to 90%.

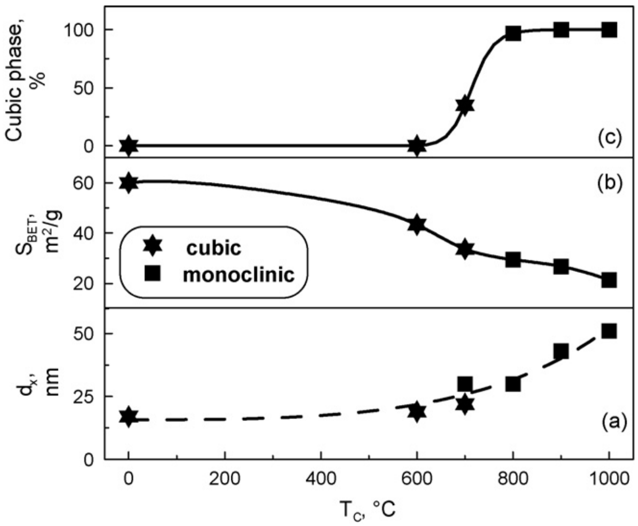

Fig. 4. The dependences of average crystalline size (a), specific surface area (b) and cubic phase content from the calcination temperature of the 1.0Nd:Y_2O_3 powder.

It was detected that the preliminary calcination of the powder lead to formation of strong agglomerates, which can not be destroyed by the intensive ultrasound (Fig. 5) as contrasted to weakly agglomerated initial powder (Fig. 1). Fig. 5 presents a micrograph of strongly agglomerated powder, calcined at 1000 °C.

It turned out that using of the preliminary transformed to the cubic phase powders allows to fabricate uniform, crackless compacts as well as ceramics. As average particle size increases the interparticle friction decreases leading to higher densities of the compacts (Fig. 6a). This set of the samples was compacted under the same conditions, at ~0.3 GPa, followed by sintering in dilatometer at 1525 °C, i.e. the shrinkage was investigated at

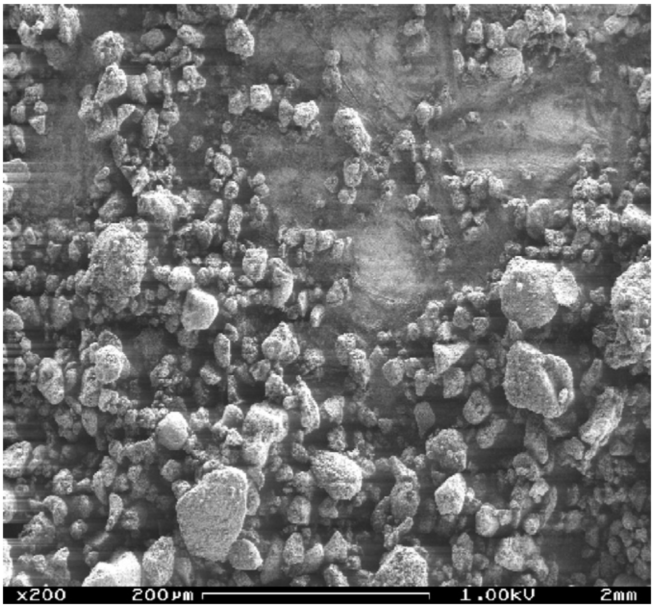

Fig. 5. SEM micrograph of 1.0Nd:Y_2O_3 powder, after calcination at 1000 °C and ultrasonic treatment.

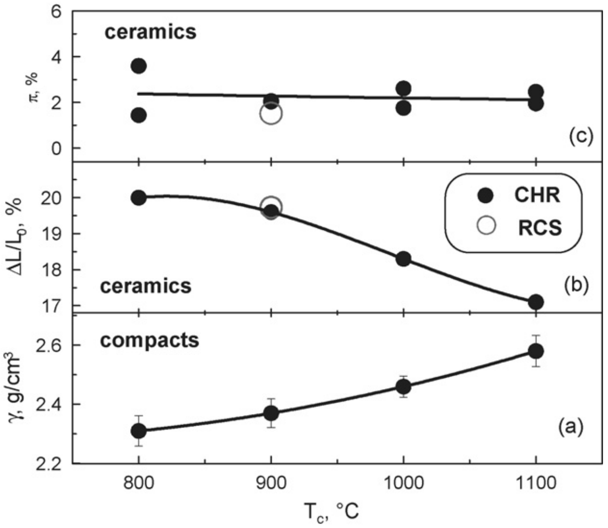

Fig. 6. The influence of the preliminary calcination temperature of the 1.0Nd:Y_2O_3 powder on its compaction (a), linear shrinkage (b) and porosity of the sintered ceramics (c).

starting and intermediate stages of sintering. X-ray diffraction analysis showed (Fig. 3d) that sintered ceramics was a single-phase solid solution of Nd in the cubic lattice of Y_2O_3. The X-ray diffraction density of the obtained material was 5.052 g/cm^3.

The increase of the starting powder calcination temperature led to the decrease in the relative shrinkage of the samples during sintering (Fig. 6b). This is explained by the increasing density of the green bodies (Fig. 6a) rather than by variation of the thermal treatment conditions. The sintering in the RCS mode did not result in essential changes of the material shrinkage (hollow cycle in Fig. 6b). The apparent average porosity of the final ceramics, measured by the hydrostatic immersion of the samples, did not depend on the calcination temperature and was about 2% (Fig. 6c). The average crystalline size, determined from the micrographs analysis was about 1–2 μm. The investigations of the sintered samples by AFM and SEM showed that the variation of the preliminary calcination temperature of the powder from 800 to 1100 °C did not influence essentially on the microstructure of its surface or fracture and that the sintering temperature of 1525 °C was not enough for the formation of poreless structure (Fig. 7a).

In this connection a set of samples was sintered in vacuum for 1 h at temperatures of up to 1700 °C. It was shown that the ceramics with well-formed boundaries and the porosity of about 1% could be fabricated already at 1630 °C (Fig. 7b), although in order to obtain the non-porous ceramics it was necessary to increase the sintering temperature.

As a result of 3.3Nd:Y_2O_3 1 h sintering at 1700 °C almost full dense ceramics, with average crystalline size of 30–40 μm and single pores less than 0.5 μm in diameter (Fig. 7c) was obtained. X-ray diffraction analysis showed (Fig. 3e) that the ceramics was a solid solution of Nd in the cubic yttria with the lattice constant of 10.6212 ± 0.005 Å. According to the optical tests, the obtained ceramics was about 40% transparent at 633 nm wavelength. This data is a little less than that obtained in[5,7] for the samples with the same thickness. Due to the surface defects

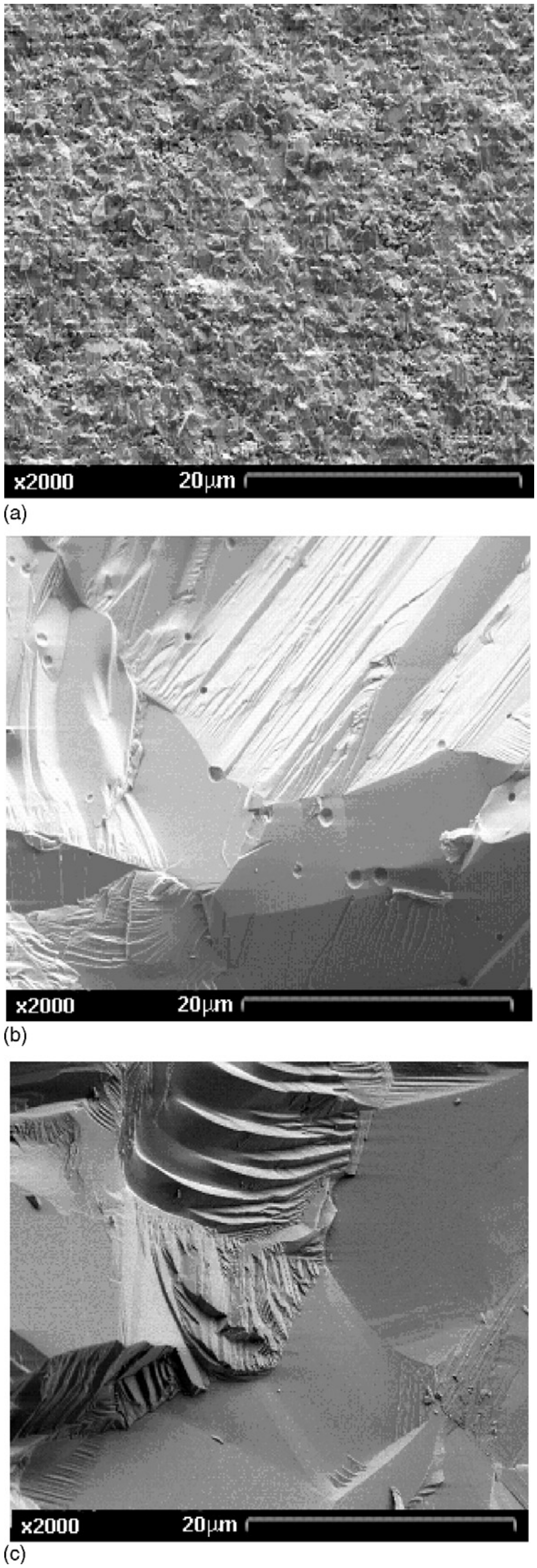

Fig. 7. SEM micrographs of the 1.0Nd:Y_2O_3 ceramics fracture, sintered at 1525 °C (a) and 3.3Nd:Y_2O_3 ceramics fractures, sintered at 1630 °C (b) and 1700 °C (c).

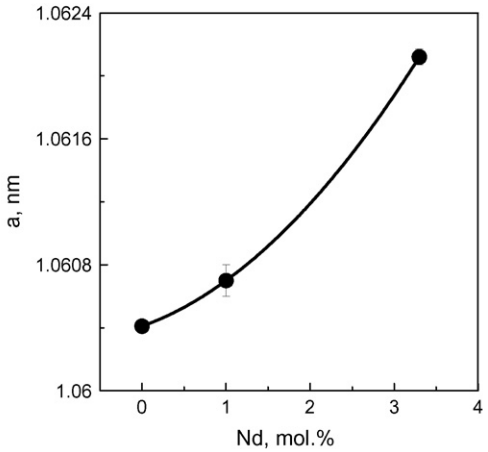

Fig. 8. The dependence of 1.0Nd:Y_2O_3 lattice constant from Nd content.

the sufficient beam scattering can be one of the main reasons of such poor data, that is why the surface of the samples needs to be improved.

The lattice constant measurements of the obtained Y_2O_3 ceramics with different Nd content and the large-crystal pure Y_2O_3 powder were made. Fig. 8 shows that the introduction of up to 3.3 mol% of neodymium into yttrium oxide results in non-linear increase of its lattice constant by tenths of percent.

Its known that during the formation of solid solution of additive in the basic oxide the following factors can influence the lattice constant: the ratio of atomic radii of the elements, the amount of oxide vacancies and the length of valent bindings of the input ion. In given case the increase of lattice constant is explained by the introduction of an additive with larger atomic radius into the basic oxide ($R_{\mathrm{Nd}} = 1.821$ Å versus $R_{\mathrm{Y}} = 1.803$ Å). Doping of the basic oxide with the large amount of Nd_2O_3 (3.3 mol%) results in mutual influence of neighbor Nd-ion fields and, as follows, there is a disruption of linear dependence of the lattice constant from the amount of inserted additive (Fig. 8).

4. Conclusions

1. Two contents of nanosized, weakly agglomerated Nd:Y_2O_3 powders with monoclinic lattice type were obtained. The investigation of phase transition showed that the powder is almost completely transformed to cubic modification after 1 h of calcination at 800 °C. The powder calcination at 1000 °C decreased the specific surface area from 60 down to 21 m^2/g and increased the crystalline average size from 17 up to 51 nm.
2. The transformation of the starting powder to the cubic modification, annealing of the compacts in air (1200 °C) and sintering in vacuum for 1 h at 1700 °C allowed to fabricate optically transparent ceramics with well-formed boundaries, average crystalline size of 30–40 μm and vanishingly small porosity with pore size less than 0.5 μm.

Acknowledgement

This work was supported by the Presidium of the Russian Academy of Science, project no. 10002-251/p-02/043-349/2004 04-087.

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