Laser ablation synthesis and characteristics of Tm-doped Gd$_2$O$_3$ nanoparticles

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Abstract. Synthesis of nano-sized particles of thulium-doped gadolinium sesquioxide is reported. The nanopowder was obtained by laser ablation of solid target composed of a mixture of Tm$_2$O$_3$ and Gd$_2$O$_3$ powders using radiation of pulse-periodical CO$_2$ laser. Morphological features, structural characteristics of nanoparticles and their densification behavior were investigated. It was shown that the as-synthesized nanopowder consists of loosely agglomerated particles with spherical shape and a diameter from 10 to 40 nm. It was revealed that the obtained sample is in the form of solid solution of Tm$_2$O$_3$ in Gd$_2$O$_3$ with monoclinic crystalline phase exhibiting the following lattice parameters: $a=14.095$ Å; $b=3.571$ Å; $c=8.758$ Å; $\beta=100.182$ °. Using X-ray diffraction analysis it was determined that, as opposed to other rare-earth sesquioxides (for instance, Y$_2$O$_3$ and Lu$_2$O$_3$), the phase transformation of monoclinic modification into cubic modification was not observed under thermal treatment at a temperature up to 1200 °C. This was also confirmed by an absence of stepwise variation in density of Tm:Gd$_2$O$_3$ compact which was evident for Gd$_2$O$_3$ sample prepared from powder with cubic phase and micro-sized particles.

1. Introduction

In recent years optical materials based on rare-earth sesquioxides doped with Yb$^{3+}$, Tm$^{3+}$ or Er$^{3+}$ have attracted considerable interest owing to potential utilization as gain media of high-power solid-state lasers [1]. Compared to Y$_2$O$_3$, Lu$_2$O$_3$ and Sc$_2$O$_3$ gadolinium sesquioxide (Gd$_2$O$_3$) of cubic modification possess relatively low phonon energy ($\nu_{\text{max}}=569$ cm$^{-1}$) [2] which can reduce undesirable multiphonon relaxation rates. However, polymorphic phase transition from the cubic phase into the monoclinic phase at the temperatures of about 1300 °C induces inability of melt growth and sintering of transparent ceramics using traditional methods. Therefore insufficient attention has been paid to the fabrication and investigation of optical materials based on cubic Gd$_2$O$_3$.

In turn, the utilization of ultrafine powders exhibiting high surface free energy (sinterability) and modern consolidation technologies enabled access to the synthesis of high-melting point polycrystalline materials such as MgAl$_2$O$_4$, Y$_2$O$_3$ and Y$_2$Al$_5$O$_{12}$ with good optical quality and submicron-grained structure at the temperatures not higher than 1300 °C [3–7]. In this work we report on the synthesis of nano-sized particles based on Gd$_2$O$_3$ by laser ablation of solid target in air flow and investigation of their morphology, crystalline structure and densification behavior.
2. Materials and methods

Nano-sized particles of Tm-doped Gd$_2$O$_3$ were synthesized in the Institute of Electrophysics UrB RAS by laser ablation of the corresponding solid target by radiation of pulse-periodical CO$_2$ laser “LAERT”. The details of experimental setup were described elsewhere [8]. In order to prepare laser target for ablation, Tm$_2$O$_3$ and Gd$_2$O$_3$ powders (99.99 mass%, Lanhit Company, Russia) composed of micro-sized particles were dry mixed together for 24 h to form Tm$_{0.1}$Gd$_{1.9}$O$_3$ mixture. The obtained blend was then compacted into cylindrical-shaped target with a diameter of ~66 mm by uniaxial static pressing at 10 MPa and pre-sintered at 1100 °C for 5.5 h in air. Typical laser parameters during the synthesis of nanopowder were as follows: pulse energy – 0.9 J, pulse duration – 330 μs, pulse repetition rate – 500 Hz, peak power – 7 kW, average power – 450 W. The laser beam was focused into 0.75 mm × 0.9 mm-sized elliptical spot by a KCl lens with a power density of 1.3 MW/cm$^2$. The linear velocity of laser beam movement was 35 cm/s. The production rate of nanopowder was 19 g/h.

The morphological features of the as-synthesized nanoparticles was observed using a JEOL JEM 2100 (JEOL Ltd., Japan) transmission electron microscope (TEM). The chemical composition of the nanopowder was analyzed using an Optima 2100 DV inductively coupled plasma mass spectrometer (ICP MS, Perkin Elmer, USA). The phase composition of nanopowder samples was examined by an X-ray diffractometer Bruker D8 Discover (Bruker AXS, Germany) using Cu Ka radiation. In order to investigate densification behavior, a round 700 mg of the as-obtained nanopowder were uniaxially pressed at 50 MPa to form 8-mm-diameter and about 4-mm-height pellet with density of about 3.22 g/cm$^3$. The compact was heated up to 1550 °C with a heating rate of 3 °C/min using a horizontal using a dilatometer NETZSCH DIL 402C (NETZSCH, Germany). Another powder compact with a density of 4.08 g/cm$^3$ was prepared from micro-sized Gd$_2$O$_3$ particles by uniaxial pressing at 200 MPa for comparison.

3. Results and discussion

Inductively coupled plasma mass spectrometry (ICP MS) was carried out to determine the chemical compositions of the as-synthesized Tm:Gd$_2$O$_3$ nanoparticles and possible deviation with respect to the composition of laser target. According to ICP MS analysis, the compositions of nanopowder and the corresponding laser target were Tm$_{0.08}$Gd$_{1.92}$O$_3$ and Tm$_{0.102}$Gd$_{1.898}$O$_3$, respectively. A slight deviation from the desired ratio is probably due to the difference in the evaporation rates of Tm$_2$O$_3$ and Gd$_2$O$_3$.

Figure 1 shows transmission electron microscopy image of Tm:Gd$_2$O$_3$ nanopowder. One can see that the particles are weakly agglomerated, have mostly single-crystalline structure and spherical shape while their size is in the range from 10 to 40 nm.
Figure 1. TEM image showing morphology of Tm:Gd₂O₃ nanopowder synthesized by laser ablation.

Figure 2 shows X‐ray diffractograms of the as-synthesized and calcined Tm:Gd₂O₃ nanoparticles in the 2θ range between 20° and 65°. The observed diffraction patterns can be well indexed to the monoclinic phase of Gd₂O₃ (PDF No. 00-042-1465), space group C2/m irrespective of the calcination temperature (Table 1). The substitution of Gd³⁺ cations for Tm³⁺ cations in the Gd₂O₃ matrix leads to a certain lattice disorder and compression of crystalline structure because the effective ionic radius of Tm³⁺ (0.88 Å) is smaller than that of Gd³⁺ (0.94 Å). Consequently, the diffraction peaks of the Tm₀.₀₈Gd₁.₉₂O₃ solid solution slightly shift toward large angle side with respect to undoped Gd₂O₃.
According to our previous works [9,10], rare-earth sesquioxides such as Y₂O₃ and Lu₂O₃ synthesized by laser ablation can be fully converted from the metastable monoclinic phase (B-modification) into the cubic phase (C-modification) by calcination at 900–1100 °C. The transformation B→C was observed in Gd₂O₃ under specific experimental conditions sustaining alternative routes of phase conversion including water, high pressure or starting materials synthesized by uncommon approaches while the opposite conversion C→B is occurred at a temperature of about 1200 °C [11-14]. This may mean that in the case of Gd₂O₃ the cubic structure is metastable rather than the monoclinic one. This fact predetermined the impossibility of fabricating highly transparent ceramics from the synthesized batch of Tm:Gd₂O₃ nanopowder since the refractive index of such polycrystalline material will be anisotropic leading to light scattering at the grain boundaries due to a different crystallographic orientation of each grain. This problem can be solved by achievement of an amorphous state of synthesized particles by reducing their characteristic sizes down to ~5 nm with the subsequent transformation into the cubic modification during heat treatment [15]. Particle size of laser-ablated nanopowders can be controlled by increasing the velocity of buffer gas or decreasing the pressure in the evaporation chamber, which requires additional investigations.

Figure 2. X-ray diffraction patterns of the as-synthesized and calcined Tm:Gd₂O₃ nanopowders.
Table 1. X-ray diffraction data of Tm:Gd$_2$O$_3$ nanoparticles before and after calcination.

| Heat treatment     | Crystalline phases                                             | Lattice parameters$^a$                                      |
|--------------------|----------------------------------------------------------------|-----------------------------------------------------------|
|                    | Solid solution of Tm$_2$O$_3$ in Gd$_2$O$_3$ with monoclinic phase, space group C2/m | a=14.095 Å; b=3.571 Å; c=8.758 Å; β=100.182 °; CSR=23 nm; ρ=8.35 g/cm$^3$ |
| 900 °C / 3 h       | Solid solution of Tm$_2$O$_3$ in Gd$_2$O$_3$ with monoclinic phase, | a=14.091 Å; b=3.570 Å; c=8.758 Å; β=100.182 °; CSR=53 nm; ρ=8.35 g/cm$^3$ |
| 1100 °C / 3 h      | Solid solution of Tm$_2$O$_3$ in Gd$_2$O$_3$ with monoclinic phase, | a=14.087 Å; b=3.570 Å; c=8.756 Å; β=99.99 °; CSR=70 nm; ρ=8.41 g/cm$^3$ |
| 1200 °C / 3 h      | Solid solution of Tm$_2$O$_3$ in Gd$_2$O$_3$ with monoclinic phase, | a=14.079 Å; b=3.571 Å; c=8.752 Å; β=99.99 °; CSR=150 nm; ρ=8.36 g/cm$^3$ |

$^a$ CSR – coherent scattering region.

The dependences of linear shrinkage and shrinkage rate on temperature for compacts prepared from laser-ablated Tm:Gd$_2$O$_3$ nanoparticles and micro-sized Gd$_2$O$_3$ powder are presented in Figure 3. A sharp decrease in the linear dimensions of the Gd$_2$O$_3$ sample (Fig. 3b) starts at 750 °C and the maximum shrinkage rate is realized at 1290 °C where the shrinkage is -8.1%. A noticeable change in the linear size in the vicinity of this temperature is associated with a stepwise increase in the density of compact due to the phase transformation of the Gd$_2$O$_3$ micro-sized powder from C-modification ($\rho=7.41$ g/cm$^3$) to B-modification ($\rho=8.35$ g/cm$^3$). On the shrinkage curve, this process appears as an abrupt dip. In turn, for laser-ablated Tm:Gd$_2$O$_3$ nanoparticles, such phenomena are not observed (Fig. 3a) confirming the absence of any phase transformations with an increase in temperature. Densification of nano-sized particles starts at ~250 °C, much earlier than in the previous case and almost completely ends at around 1150 °C. The maximum change in linear dimensions is -28.2%, which is more than 3 times higher than the similar parameter for micro-sized particles.

Figure 3. Densification behaviour of powder compacts prepared from laser ablated Tm:Gd$_2$O$_3$ nanoparticles (a) and commercial Gd$_2$O$_3$ powder with micro-sized particles (b).

4. Conclusion

Nano-sized particles of Tm$_{0.08}$Gd$_{1.92}$O$_3$ solid solution with the monoclinic phase were synthesized by laser ablation of solid target. Unlike Y$_2$O$_3$ and Lu$_2$O$_3$, transformation of the monoclinic phase into the cubic phase was not observed in laser-ablated Tm:Gd$_2$O$_3$ nanoparticles upon calcination at a temperature of 1200 °C. Nevertheless, the as-synthesized nanopowder exhibited high sinterability with respect to micro-sized particles and the value of linear shrinkage reached as high as -27.4% at 1150 °C corresponding to a relative density of about 89.2%. Thus, the obtained results indicate that the fabrication of highly transparent Tm:Gd$_2$O$_3$ ceramics with cubic structure would require to develop a productive method for the synthesis of ultrafine (~5 nm) nanoparticles in amorphous state.
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