Influence of carbon contamination on transparency of reactive SPSed Nd$^{3+}$:YAG ceramics

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Abstract. Influence of carbon contamination from the paper and dies on structural-phase state and transparency were studied for SiO$_2$-doped Nd$^{3+}$:Y$_3$Al$_5$O$_{12}$ ceramics obtained via reactive spark plasma sintering (SPS). It is shown that the transparency of post-annealed ceramics is sensitive to the SPS temperature. Since the swelling effect is related to the amount of the carbon phases as well as their composition and depth of location, the degradation becomes remarkable with the temperature increasing above critical for SiO$_2$-doped Nd$^{3+}$:Y$_3$Al$_5$O$_{12}$ system. Ceramics fabricated at 1500°C contains SiC and SiOC-based impurity phases, which are relatively stable for post-annealing. Removal of generated defects is possible for ceramics fabricated at relatively low temperatures (~1350°C).

1. Introduction

Recently, we have suggested an original approach to obtain fine-grained Nd$^{3+}$:Y$_3$Al$_5$O$_{12}$ (Nd$^{3+}$:YAG) ceramics via reactive SPS of nanopowders in the Y$_2$O$_3$−Nd$_2$O$_3$−Al$_2$O$_3$ oxide systems with controlled particle size distribution. This route allows implementing simultaneously external pressure, particle surface curvature and chemical reactions as driving forces of sintering to obtain uniform highly dense microstructure [1]. XRD analysis showed that carbon contamination occurred in the garnet Nd$^{3+}$:YAG ceramics depends on the SPS conditions. Carbon phases can arise from the paper and dies that are essential components and are widely used in the SPS treatment [2, 3].

SPS processing, especially at high temperatures, leads to the carbon contamination causing serious problems for the final materials. Although the contamination has already been reported in earlier studies, the SPS parameter dependent contamination behavior is still not fully understood [2–4]. In order to fully utilize the SPS technique, particularly for industrial applications, the suppression of the carbon contamination is important [5, 6]. Therefore, the purpose of present paper is to examine the carbon contamination behavior under reactive SPS conditions using a polycrystalline highly-doped garnet 4 at% Nd$^{3+}$:YAG as a model system. The influence of a carbon phases on structural-phase state of the obtained ceramics as well as the transparency of the samples sintered at different temperatures are discussed.
2. Experimental

High purity commercial α-Al₂O₃ (>99.99%, Baikowski; d=0.15-0.3 μm); Y₂O₃ (99.999%, Alfa Aesar; d=5 μm) and Nd₂O₃ (>99.99%, Alfa Aesar; d=2-5 μm) powders were used as starting materials. 0.5 wt% of tetraethyl orthosilicate (0.14 wt% SiO₂ (≈1.43 at% Si⁴⁺)) was added as sintering aid. Powders were weighted to fit the chemical composition of 4 at% Nd³⁺:YAG (2.88Y₂O₃:0.12Nd₂O₃:5Al₂O₃), mixed with ethanol and then milled with Al₂O₃ balls using a Pulverisette 5/4 (Fritsch GmbH, Germany) planetary ball mill. Then the powder mixture was dried, sieved, and loaded into a graphite die with an inner diameter of 15 mm, the internal surface of which was covered with graphite sheet. Sintering experiments were done on a SPS-515S (Dr. Sinter*LAB™, Japan) unit in the temperature range of 1350-1500°C and dwell time 5 min (under pressure 30 MPa). After sintering, the ceramic samples were being annealed for 1 hour in air at 900°C to recover oxygen vacancies and to remove residual stress. For testing optical transmittance, the samples were mirror polished on both surfaces with different grade of the diamond slurries.

The room temperature transmittance spectra of Nd³⁺:YAG specimens were measured in the range of 0.2 to 1.1 μm with a Lambda-35 spectrophotometer (Perkin-Elmer, USA). The refractive indices of Nd³⁺:YAG ceramic for various wavelengths were calculated using Sellmeier’s dispersion equation with the coefficients for it being fitted using data points from work [7]. In-line transmissions have been referred to a constant sample thickness of 1 mm, using the relationship derived from the Beer–Lambert law. X-ray photoelectron spectroscopy (XPS) data were collected from sample’s surface in the high vacuum double-chamber system (Specs, Germany) with a hemispherical electrostatic analyzer Phoibos-150 (vacuum in camera was 10⁻⁷ Pa, the radiation energy was 1253.6 eV (Mg Kα), the accuracy of the binding energy determination is 0.2 eV, thickness of the analysed layer 5 nm). For carbon-containing samples, electron binding energy calibration (E₀) was performed based on the intrinsic standard method with the C1s level from adsorbed hydrocarbon contamination (E₀=285.0 eV) as a reference. To remove the surface layer (to 5 nm), argon ion (5000 eV) etching was used with the calibration of E₀ for the cleaned sample (without organic contamination) based on Al2p (E₂p=74.2 eV) level as a reference. The surface composition of all samples was determined using photoelectron lines area ratio taking into account their sensitivity factors. The errors of absolute values of element atomic concentration, calculated without using etalons, may be up to 20%.

3. Results and discussion

Figure 1a shows in-line transmittance of as-sintered and post-annealed 4 at% Nd³⁺:YAG ceramics obtained by reactive SPS at temperature range 1350-1500°C. Sintering at the temperatures of 1350-1500°C has practically no effect on ceramics’ transmittance in the near IR spectral range (transmittance T₁₅₀₀=63.5±67.8% for 1.0 mm thickness samples). Consequent annealing in oxygen atmosphere at 900°C for 1 hour leads to increased transmittance of ceramics prepared at 1350°C: from 35.5 to 40.1% (for 600 nm), and from 63.5 to 67.7% (for 1064 nm). However, transmittance of samples obtained at higher temperatures is reduced significantly (Figure 1a). For example, post-annealing of ceramics prepared at 1500°C downgrades transmittance from 45.1 to 4.1% (for 600 nm), and from 67.8 to 33.5% (for 1064 nm). This can be attributed to pore coalescence and formation of additional pores, local microcracks and grain-boundary defects when removing carbon traces that penetrated into the ceramics bulk. Since these processes are related to the amount of the carbon phases, their composition and depth of its location, the degradation becomes remarkable within increasing temperature above critical for that system. Such effects related to removal of residual carbon particles by annealing and swelling have been recently demonstrated for other oxide ceramics [2-6, 8-10]. In turn, lower temperatures enable carbon to penetrate only into the subsurface of the ceramics. The gaseous CO₂/CO phases near the surface areas may be eliminated along the grain boundaries.

We have done XPS analysis on Nd³⁺:YAG polished surfaces (reactive SPS at 1350°C and 1500°C for 5 min and post-annealed at 900°C for 1 hour) to estimate the influence of carbon contamination on structural-phase state and transparency of garnet ceramics. Qualitative and quantitative analysis has
been performed for ceramics before (“1350” and “1500”) and after (“1350c” and “1500c”) ion etching of the surface. Additionally, data on initial 2.88Y2O3·0.12Nd2O3·5Al2O3 powder mixture and carbon paper after SPS were used as a reference (Figure 1b, Table 1).

Samples’ chemical composition was identified using C1s, O1s, Y3d_{5/2}, and Al2p levels. Neodymium signal was not detected, because the most intense line (Nd3d_{2,3}/spin-orbital doublet) is shaded by Auger-line C_{KLL}. Analysis of less intense Nd4d (~120 eV) line shows Nd concentration is less than 1 at%. A small amount of Si arising from the sintering aid was not taken into account either.

### Table 1. The surface chemical composition and position of resolved lines.

|        | Initial powder | Carbon paper | “1350” | “1350c” | “1500” | “1500c” |
|--------|----------------|--------------|--------|---------|--------|---------|
| C1s    |                |              |        |         |        |         |
| E_b (eV) | 285.0*         | 284.5*       | 285.0* | –       | 285.0* | 285.0*  | 283.6   |
| e (at%) | 24.6           | 95.5         | 31.2   | –       | 48.1   | 2.2     |
| O1s    |                |              |        |         |        |         |         |
| E_b (eV) | 530.8          | 531.4        | 530.1  | 529.7   | 530.3  | 530.0   |
| e (at%) | 42.5           | 4.5          | 36.8   | 52.3    | 27.9   | 50.8    |
| Y3d_{5/2} |              |              |        |         |        |         |         |
| E_b (eV) | 158.0          | 156.2        | 157.6  | 157.8   | 157.9  | 157.9   |
| e (at%) | 10.3           | –            | 11.9   | 19.4    | 8.2    | 18.9    |
| Al2p   |                |              |        |         |        |         |
| E_b (eV) | 74.5           | –            | 74.2   | 74.2*   | 74.2   | 74.2    |
| e (at%) | 22.6           | –            | 20.1   | 28.3    | 15.8   | 28.1    |

* – Indicated values were used to calibrate the energy scale

According to XPS, surface concentration of carbon is 2.2 at% for ceramics “1500c” (Figure 1b, Table 1). Intense line C1s in the XPS spectrum of ceramics “1500c” can be considered as a sum of two components: 283.6±0.2 eV, which can be attributed to C1s silicon oxycarbide-based phases SiOxC_{y} (where x+y=4; x,y>0) [11] or to C1s of silicon carbide SiC [12]; and 285.0 eV corresponding to residual hydrocarbon traces. It is noteworthy that contribution of the first component is prevailing. Formation of SiOxC_{y} phases is also proved by Si2p line in the spectrum of ceramics “1500c” with E_b=102.2±0.2 eV and e<1 at% [11]. Possible coexistence of yttrium, aluminum, and silicon carbides is unlikely. For example, energy of C1s line of Al2C_{3} is 282.2 eV [13], while data on C1s XPS spectra of YC, Y_{2}C_{3}, YC_{2} is absent. Thus, high sintering temperatures combined with external load leads to formation of impurities with Si–C bonds: SiC and SiOC-based phases [14]. Silicon carbides oxidation occurs at temperatures of 950-1700°C, whereas graphite oxidizes at 600-700°C depending on graphite
type and its particle size. At the same time, sample “1350c” contains less than 1 at% of carbon, therefore, extraction of C1s line is rather difficult (Table 1, Figure 1b). Formation of disordered carbon phases, such as glassy carbon and/or graphite oxide (GO) phases from the paper and dies, is known to occur in the absence of chemical interaction between carbon and silicon (similarly to [5, 6]).

In conclusion, to minimize contamination with carbon, it is advisable to perform sintering at lower temperatures and at longer dwell times, because diffusion coefficient grows exponentially with temperatures and linearly with time. Experimental proof of these assumptions will be published elsewhere in detail.

4. Conclusions
Neodymium doped yttrium aluminum garnet 4 at% Nd3+:YAG transparent ceramics were obtained by the reactive SPS using commercial α-Al2O3, Y2O3, and Nd2O3 powders as starting materials, and SiO2 as a sintering aid. The influence of carbon phases caused by the paper and dies on structural-phase state and transparency of as-sintered at 1350-1500°C for 5 min, and post-annealed at 900°C for 1 hour samples are examined.

The transparency of post-annealed ceramics is sensitive to the SPS temperature. Annealing increases transmittance of ceramics prepared at 1350°C: from 35.5 to 40.1% (for 600 nm), and from 63.5 to 67.7% (for 1064 nm). However, thermal treatment reduces transmittance for ceramics prepared at 1500°C: from 45.1 to 4.1% (for 600 nm), and from 67.8 to 33.5% (for 1064 nm). According to XPS analysis ceramics fabricated at 1500°C contains SiC and SiOC-based impurity phases, which are relatively stable to post-annealing. Removal of generated defects, such as residual porosity and carbon-contained impurities, is possible for SiO2-doped Nd3+:YAG ceramics fabricated at relatively low temperatures (~1350°C).

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