Spark plasma sintering of transparent YAG:Ce ceramics with LiF flux

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Abstract. Transparent yttrium aluminum garnet (YAG) ceramics doped with cerium ions (Ce^{3+}) were successfully synthesized using the spark plasma sintering (SPS) process at a temperature of 1600 °C, isothermal exposure 10 minutes, pressure 100 MPa and a heating rate 10 °C/min from a mechanical mixture of powders of yttrium, aluminum, and cerium oxides. Transmittance in the visible range for 1 mm thick samples is above 40 %; in the near infrared is above the 60 %. Vickers hardness was 15±1.05 GPa. The optimal SPS conditions have been discussed and suggested in order to obtain a good combination of density and transmittance.

1. Introduction

Yttrium-aluminum garnet ($Y_3Al_5O_{12}$, YAG) doped with rare earth (RE) ions or transition metals (TM) is well known optical material with physical integrity, good chemical stability, perfect thermal and optical characteristics. It is used for manufacturing scintillators and active elements of near-and mid-IR solid-state lasers [1, 2].

In recent years, yttrium-aluminum garnet doped with cerium ions (YAG:Ce) phosphors and luminescent transparent ceramics have been actively used for white light-emitting diodes (wLED) production. Modern commercial wLEDs is a combination of a GaN semiconductors which generate blue emission and coated by the mixture of YAG:Ce^{3+} phosphors with optically transparent organosilica polymer or epoxy resin [3, 4].

Transparent ceramics considered as the most promising in this case due to practical application and benefits for further wLED technology development. There are several advantages over phosphor powders such as high mechanical, optical, and luminescent properties. The YAG:Ce ceramics have relatively high thermal conductivity, thermal and chemical resistance. It potentially can be solve the well-known problem of optically transparent coatings degradation [5] and can be used in conjunction with high-power wLEDs [4, 6].

Currently transparent YAG:Ce ceramics produced by various methods. More spreadable of them are cold pressing and sintering [7] or spark plasma sintering (SPS) techniques [8, 9]. SPS method is the most promising approach for transparent ceramics preparation. Since it ensures the preservation of the initial phase composition, structure, and high density of consolidated materials, close or equal to the theoretical one. It allows producing transparent ceramics in a relatively short period of time [10].

Besides, SPS technique reduces the temperature and the duration of solid-phase synthesis of YAG ceramics to a value equal to the SPS process duration [11-13].

One of the problems appearing in SPS method during the transparent ceramics fabrication is the contamination of the sintered material with carbon, which occurs due to the use of graphite tooling. To solve this problem the lithium fluoride (LiF) as a sintering flux can be used. It allows eliminating or significantly reducing the contamination degree of ceramics [14, 15].

In present work, the transparent YAG:Ce ceramics is prepared from a mechanical mixture of yttrium, aluminum, and cerium oxide powders using SPS technique. Optical and microstructural characteristics are investigated.

2. Expiremental

Mechanical mixture of chemically pure micropowders: Al_2O_3 (99.9 %, Chongqing, China), Y_2O_3 (99.9%, Chongqing, China), CeO_2 (99.9%, Chongqing, China) were used as starting materials [5]. Lithium fluoride (LiF, 99.9%, Siberian Chemical Combine, Russia) was used as sintering aid. Powders were mixed in desired stoichiometric ratio: $Ce_{0,06}:Y_{2.96}Al_5O_{12}$ with 0.25 wt. % LiF and ball milled for 48 h in ethanol. After the ball milling, the obtained suspension was dried at 80 °C for 12 hours. The dried powder mixture was ground and sieved through screen.

For YAG:Ce ceramics fabrication the SPS-515S installation (SPS SyntexInc., Japan) was used in the temperature ranges from 1400 °C to 1600 °C at heating rates 10 °C/min and 50 °C/min. The duration of isothermal curing at a given sintering temperature varied from 3 to 15 min. The static pre-pressing pressure in the graphite die was 100 MPa. The process was carried out in a vacuum at a residual pressure less than 10^{-3} Pa. The temperature during sintering was controlled by a high-temperature pyrometer at the bottom of the process hole made on the side surface of the graphite die. After the sintering, the transparent cylindrical ceramic samples with a diameter of 14 mm and a height of 1.5 mm were mechanically polished with a polishing machine (EcoMet 300 Pro, Buehler, Germany) using Kemix diamond suspensions (Kemika, Russia). The height of the polished samples was 1 mm.

The density of the sintered YAG:Ce ceramics was determined by measuring their dimensions by a digital micrometer “Electron” (Russia) with an accuracy of 10 μm and measuring their mass by a digital balance VLTE-150 (Russia) with an accuracy of 10 mg. In order to gain statistically reliable data, 5 samples were obtained by each processing routes.

The microstructure of the YAG:Ce ceramics was analyzed by Leo Evo 50 scanning electron microscope (CarlZeiss, Germany).

X-ray phase analysis was performed on an XRD-7000S diffractometer (Shimadzu, Japan). The results were deciphered using the international crystallographic database "PDF-4" and the freely distributed “PowderCell 2.4” software.

The optical properties were studied in the ultraviolet, visible, and near-infrared spectral regions using a SF-256 UVI two-beam scanning spectrophotometer (Lomo-Photonics, Russia).

The study of the elastoplastic properties and microhardness of YAG:Ce ceramics was carried out by the method of indentation with a diamond pyramid by a DUH-211S ultramicrohardness tester (Shimadzu, Japan) at a load of 1.96 N.

3. Results and discussion

The results of the density and SPS modes of YAG:Ce ceramics are presented in Table 1.

Table 1. The SPS modes and the density values of YAG:Ce ceramics

Processing route	Sample	*t*, min	*T*, °C	*v*, °C/min	*ρ*, %
	1.1		1400		95.3±0.5
No 1	1.2	3	1500	50	95.6±0.5
	1.3		1600		95.9±0.5
No 2	2.1	3	1400		95.3±0.5

	2.2	10			96.6±0.5
	2.3	15			96.8±0.5
	3.1	15	1400		97.1±0.5
No 3	3.2	15	1500	10	97.3±0.5
	3.3	15	1600		98.8±0.5

At high heating rates of SPS mode (Processing route No. 1 and No. 2) did not lead to sufficient compaction of the YAG:Ce ceramics. The relative density consist no more than 96.8 % of the theoretical value (4.56 g / cm^3) [16]. For obtaining a transparent material in wide spectral range this density value is not enough.

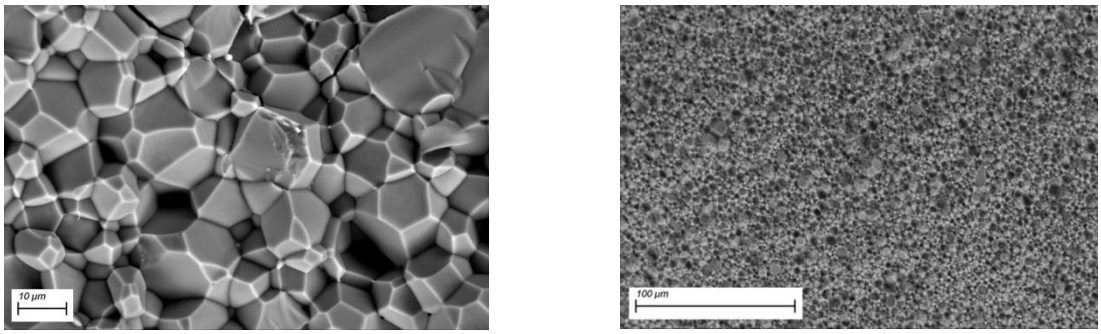
However at low heating rates of SPS mode (Processing route No. 3 in Table 1) allowed to obtain ceramics with relative density up to 98.8% of the theoretical value. The YAG:Ce ceramics fabricated at temperature 1600 °C and a heating rate 10°C/min were transparent from UV to near IR spectral region. Photographs of YAG:Ce ceramics (series No. 3) sintered at different temperatures are shown in Figure 1.

(a) (b) (c)

Figure1. Samples of YAG:Ce ceramics manufactured by SPS at low heating rates and temperatures (a) 1600 °C, (b) 1500 °C, (c) 1400 °C

Further studies of the microstructure, phase composition, optical and mechanical properties of YAG:Ce ceramics were carried out only for the sample prepared at 1600 °C.

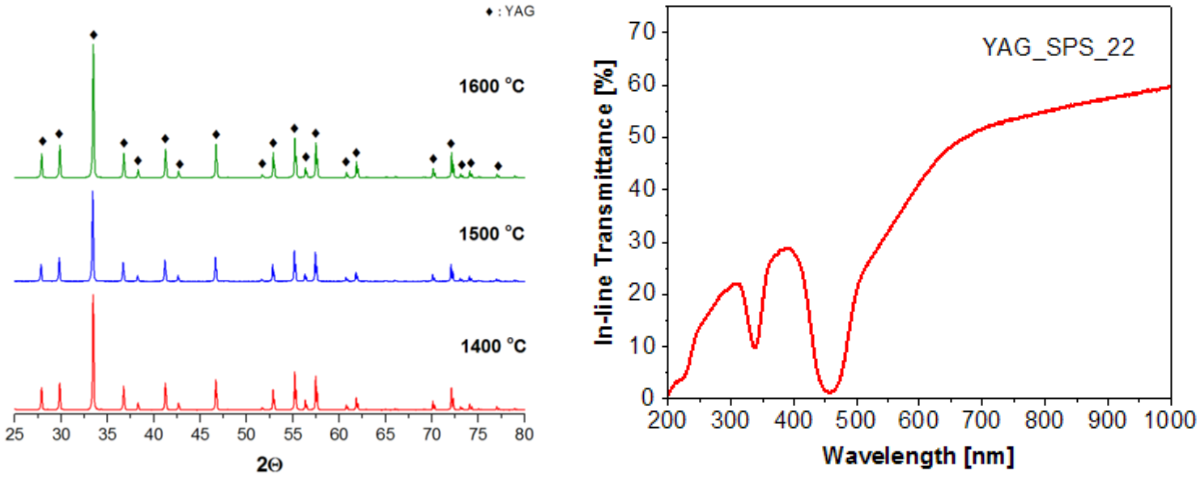
Figure 2 shows a typical SEM-images of the side surface of the cleavage of YAG:Ce ceramics. The destruction of ceramics occurs mainly by the intercrystalline mechanism. The grains size of the ceramics varies from 293 nm to 12.4 μm, which is comparable to the particle size of the original powder mixture. The average grain size was 5.3 μm.



(a) (b)

Figure 2. SEM-image of a polished surface of YAG:Ce-ceramics sintered at temperature 1600 °C: a) 10μm b) 100 μm

X-ray phase analysis has shown that studied ceramics consist of cubic phase of yttrium-aluminum garnet. The presence other phases in the YAG:Ce ceramics were not detected. XRD reflections did not show any shifts in position or additional phases in the sample. It indicates that the cerium was completely inserted into the garnet structure. The lattice parameters (12.0096 Å), mean size crystallite size (423 nm), and relative microstrain (0.000095 arb. un.) were determined. Typical reference and experimental diffractograms of the samples are shown in Figure 3a.



(a) (b)

Figure 3. (a) X-ray diffraction patterns transparent YAG:Ce - ceramics; (b) Light transmission spectrum of YAG:Ce - ceramic samples obtained by the SPS method at a temperature 1600 °C and a heating rate of 10 °C/min

The microhardness of transparent YAG:Ce ceramics was 15.01±1.05 GPa. The modulus of longitudinal elasticity at indentation was 171.5±11.71 GPa and the fluidity factor at indentation was 1.56±0.45%.

The results of the in-line transmission study of transparent YAG:Ce ceramics fabricated by the SPS method at a temperature 1600 °C and a heating rate 10 °C/min are shown in Figure 3b. The ceramics are transparent in the UV, visible, and near IR spectral regions. The short wavelength of the transmittance edge is located at 200 nm. The transmittance coefficient in the UV at 390 nm reaches 28%, in the visible range at 600 nm is 41%, and in the IR spectral range at 1100 nm is 61%, respectively. The relatively low value of transmittance coefficient in the UV spectral region comparing to the visible ones at a wavelength of 340 nm can be determined by the photoluminescence of the studied material. The excitation band of the luminescence is located in the region at 340 nm [17, 18].

4. Conclusion

As a result, a complex studies of SPSed sintered YAG:Ce ceramics from a mechanical mixture of initial oxides powders and study their microstructure, optical, and mechanical properties were carried out.

The optimal SPS technological modes were determined such as sintering temperature 1600 °C; pre-pressing pressure 100 MPa, isothermal exposure at the maximum temperature 15 min, heating rate 10 °C/min. The high values of relative density 98.8%, high optical transmittance 41% at 600 nm with elastoplastic (microhardness (15±1.05 GPa), longitudinal elastic modulus at indentation (171.5±11.71 GPa) and fluidity factor at indentation (1.56±0.45 %) for YAG:Ce ceramics were achieved. It was established that the transparent ceramics based on YAG:Ce ions fabricated using the SPS method, in the studied range of modes, is possible only at low heating rates.

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