

Density and microstructural investigation of Ce:YAG ceramic subjected to powerful ultrasonic treatment during the compaction process

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Abstract. The aim of the present work was to investigate the effect of the applied pressure, sintering temperature and ultrasonic treatment during the pressing process on the density and microstructure of translucent ceramics based on yttrium-aluminum garnet doped with cerium ions (Ce: YAG) obtained by conventional sintering of pressed compacts. The optimization of manufacturing conditions of the ceramics was carried out. It was shown that the ultrasonic treatment of initial powder in optimal sintering conditions leads to an increase in the relative density and grain size and decrease in the pore size of the sintered ceramics.

1. Introduction

Ceramics based on yttrium-aluminum garnet - $Y_3Al_5O_{12}$ (YAG) is a promising material owing to its high melting point and heat resistance, the absence of polymorphic transformations and good electrophysical properties. YAG ceramics can be used as an alternative to glasses or single crystals in devices that work at low visibility, high temperatures, aggressive environments and so on. In past decade, inorganic phosphors based on yttrium-aluminum garnet doped with trivalent cerium ions (Ce:YAG) began to be used for white light-emitting diodes (LED) [1, 2]. However, Ce:YAG-phosphors have amount of disadvantages associated with the degradation of optical and luminescence properties in the process of their use [3]. Ceramic is devoid these disadvantages. Therefore, it is highly relevant to use Ce:YAG-ceramics in white LED-technology [2, 4-10].

The sintering process of high-density ceramics is associated with the problem of keeping the initial phase composition, structure and purity of the material during the pressing process. It is due to the use of various surfactants or binder additives to achieve a higher density of the pressed material without destruction. This is a technological problem that especially relevant for materials used in optical instrumentation where the presence of impurities have a negative impact on the complex of optical-luminescent characteristics. Current problem of high-quality consolidation of Ce:YAG-ceramics can be solved by the methods of hot pressing or spark plasma sintering, however, this leads to high economic costs [2, 11]. It is relevant to use methods that do not require large economic costs and allow obtaining



ceramics with uniform density and minimal residual porosity. Such as ultrasonic and collector pressure followed by sintering [12].

In the present work, the possibility of obtaining high-density luminescent Ce: YAG ceramics by ultrasonic pressing followed by sintering in air was demonstrated, the effect of pressure, sintering temperature, and ultrasonic action on the density and microstructure of a consolidated material were investigated.

2. Experiments

Ceramic samples were sintered from a homogeneous mechanical mixture of chemically pure reagents Al_2O_3 (99.99%), Y_2O_3 (99.99%), CeO_2 (99.99%). The powder mixture was made at Chongqing University of Arts and Science (Chongqing, China).

Green bodies were prepared as by the static uniaxial pressing so by the uniaxial ultrasonic pressing [12] at pressure 100-600 MPa on automatic press IP-500AVTO (ZIPO, Russia).

The green bodies were sintered at temperatures from 1550 to 1700 °C for 8 hours in air atmosphere in muffle furnace LHT 02/18 (Nabertherm, Germany).

The sintered ceramic samples had a thickness of 1.5 – 1.7 mm and 8.5 – 9 mm in diameter. Before being characterized, the samples were polished used by polishing machine EcoMet 300 Pro (Buehler, Germany) with Polylab PRO (Kemika, Russia) diamond suspension. The density of the sintered specimens 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 sintered samples were observed by using scanning electron microscope Leo Evo 50 (Carl Zeiss, Germany) with probe microanalysis system “INCA Energy – 350” (Oxford Instruments, England).

YAG-ceramic samples were studied by X-ray diffraction (XRD) phase analysis. The XRD patterns were recorded using XRD-7000S (Shimadzu, Japan).

3. Results and discussion

Figure 1 presents the obtained dependence of the density of green bodies (black curve) and sintered at 1650°C ceramics (grey curve) on the compaction pressure.

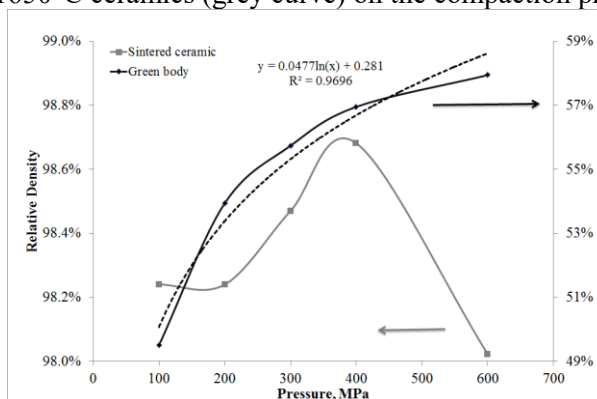


Figure 1. The dependence of the density of Ce:YAG on pressure

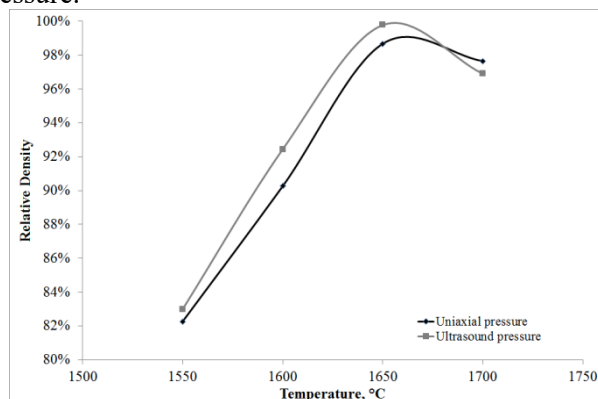


Figure 2. The dependence of the density of Ce:YAG on sintering temperature

The density of the green body with increasing pressure increases according to the logarithmic law [13, 14]. The behavior of the studied material during the densification process in a closed rigid mold with sufficient reliability (~ 97%) can be described by a logarithmic equation in a dimensionless form (1).

$$\rho = b \cdot \ln\left(\frac{P_{np}}{P_{cr}}\right) + 1, \quad (1)$$

where ρ – relative density of the green body, b – is a material constant defining densification pressure sensitivity, P_{pr} is the applied compaction pressure, P_{cr} is the critical pressure (pressure enabling compaction up to full density of the powder material). The coefficients a logarithmic equation were determined by approximating the experimental compaction curves with approximation certainty not less than 96%, the value of coefficient b for the investigated material was 0.0477.

An increase in the compaction pressure from 100 to 600 MPa leads to an increase in the density of the green body from 49.51% to 57.94%. The maximum density value (98.68%) after sintering (figure 1) is observed in ceramics obtained at compaction pressure – 400 MPa. In sintered ceramic samples obtained at compaction pressures above 400 MPa are formed the cracks that are visible to the naked eye. And in some green bodies, obtained at similar pressures lamination was observed. Apparently, this is caused by anisotropic density distribution over the volume during the compaction process of green body which leads to the accumulation of residual stresses and formation of macrodefects.

Based on the obtained results, further molding of the samples was carried out under the pressure of 400 MPa.

Figure 2 presents the obtained dependence of the density of sintered ceramics on the sintering temperature.

The maximum density value 98.7 % and 99.8% is observed for samples obtained by uniaxial and ultrasonic pressing with followed sintering at 1650 °C, respectively. An increase in sintering temperature from 1550 °C to 1650 °C leads to leads to significant rise the relative density of samples by 16.4%. Further increase in sintering temperature from 1650 °C to 1700 °C leads to decrease the relative density by 1 - 2.9%.

Table 1. Density and microstructure properties of sintered Ce:YAG-ceramic

| Sample | Relative density, % | Average grain size, μm | Average pore size, μm |
|--------|------------------------|---------------------------|--------------------------|
| 1550 | 82.26±1 | 1.95 | 0.49 |
| 1550* | 82.99±1 | 1.6 | 0.54 |
| 1600 | 90.26±1 | 2.19 | 0.62 |
| 1600* | 92.44±1 | 2.2 | 0.64 |
| 1650 | 98.68±1 | 4.2 | 1.25 |
| 1650* | 99.78±1 | 4.57 | 0.94 |
| 1700 | 97.65±1 | 15.4 | 1.8 |
| 1700* | 96.90±1 | 13.8 | 1.19 |

*Ultrasonic pressing

Figure 3 shows SEM-images of the spall microstructure of ceramics sintered at different temperatures. It was found that the fracture behavior of ceramics is changes from intercrystalline at temperatures 1550-1600 °C transcrystalline at temperatures 1650-1700 °C. This indicates an increase in the strength of grain boundaries to a value comparable to the grains strength. The measurement results of the relative density, average grain and pore size of investigated ceramics represented in the table 1.

An increase in sintering temperature from 1650 °C to 1700 °C leads to an increase average grain size of investigated ceramics from 1.95 to 15.4 μm, average pore size increase from 0.49 to 1.8 μm. This kind of the change in the average size of structural elements can be explained as follows. At sintering temperatures of 1550-1600 °C with an isothermal exposure - 8 hours and relatively low heating rates, the sintering process does not seem to be completed, and therefore the grain growth process proceeds slowly, and their size remains at the level of the agglomerates of initial powder. Density of the samples for this type of ceramics is relatively low and does not exceed 92.5 %. At sintering temperature - 1650 °C with an isothermal exposure - 8 hours, densification of sintered material occurs intensively and accompanied by decreasing pore quantitative content and grain growth. At a temperature of 1700 °C and an isothermal exposure time - 8 hours, sintering process significantly slows down, which result in a

significant grains growth without further densification of material, which leads to the transition of intergranular residual pores into the volume of grains.

The influence of ultrasonic treatment at relatively low sintering temperatures (1550-1600 °C) is weakly expressed. The effect of ultrasonic treatment can be fully evaluated at temperatures 1650 °C and 1700 °C. Thus, the residual pores average size of the samples obtained by ultrasonic pressing at sintering temperature 1650 °C on 0.31 μm less, the average grain size on 0.37 μm less and the density on 1.1% higher than that of the samples obtained by uniaxial pressing followed by conventional sintering at the same temperature. Increasing density and grain size of the sonicated ceramic samples can be explained by activation effects of ultrasonic treatment, whereby the grain growth speed is enhanced. Sonicated ceramic samples demonstrate the predominantly transcrystalline fracture behavior, while their non-sonicated analogues show intercrystalline fracture behavior.

In this context, two processes accompanying sintering can be considered: grain boundary diffusion, which leads to an increase grain size, and grain boundary sliding, which leads to decrease a pore size. Ultrasonic treatment, which has an activation effect on the green bodies, makes it possible to intensify these processes by different ways during sintering.

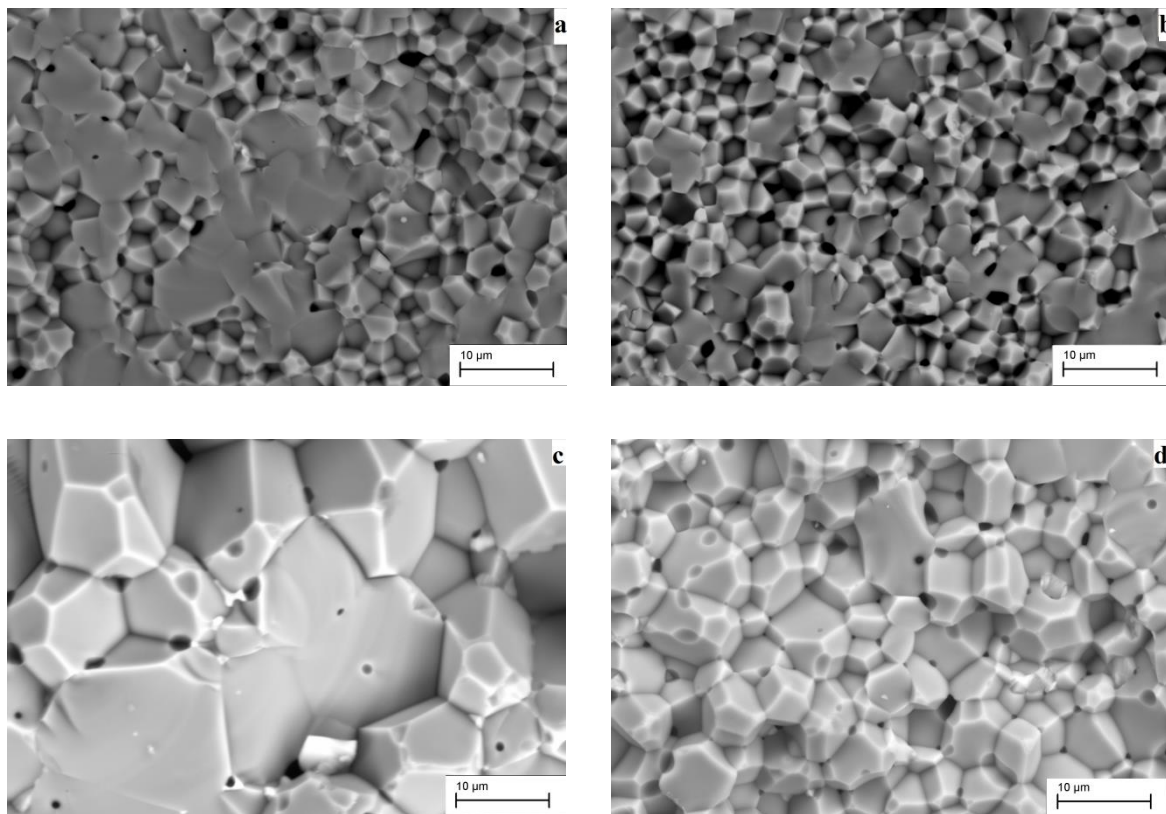


Figure 3. SEM-images of the fractured surface of ceramics sintered at (a) - 1650 °C; (b) - 1650 °C sonicated; (c) - 1700 °C; (d) - 1700 °C sonicated.

Thus, at sintering temperature - 1650 °C activation of the powder particle surface caused by ultrasonic treatment leads to a parallel intensification of two processes: grain boundary diffusion and grain boundary sliding, which increase grain sizes and decrease sizes of sonicated samples in comparison with non-sonicated samples. However, the density increase of sonicated samples sintered at this temperature indicates a slight predominance of grain boundary sliding.

Sintering at maximum temperature is accompanied by a significant acceleration of grain growth with a limited rate of pore size reduction, which indicates the dominance of the grains coalescence processes

over the processes of their grain boundary sliding. In this case, the effects of closing porosity were observed. At sintering temperature - 1700 °C relative density, average grain and pore size of sonicated ceramic samples less than those of non-sonicated ceramic samples. Thus, the ultrasonic treatment effect on these samples, in contrast to samples sintered at 1650 °C, led to a parallel decrease in both pore sizes and grain sizes. This fact also confirms the assumption that ultrasonic activation intensify grain boundary sliding makes it possible to limit the diffusion coalescence of grains at high sintering temperatures. However, a slight density decrease of the sonicated samples indicates that the pore content increased. It may be due to the effect of closing porosity mentioned above.

Obviously, ultrasonic pressing at 400 MPa, followed by sintering at a temperature of 1650 °C, is optimal condition among the investigated range, which can significantly reduce both the pore size and the value of residual porosity while maintaining grain sizes at an acceptable level.

X-ray phase analysis confirmed that ceramic samples consist of stoichiometric yttrium-aluminum garnet of cubic modification. All observed peaks are characteristic for the garnet phase.

The presence of other phases in the samples of ceramics were not detected. XRD reflections do not show any shifts in position or additional phases, indicating that the cerium were inserted completely in the structure.

4. Conclusion

High density ceramics based on Ce:YAG were produced by ultrasonic pressing at room temperature followed by conventional sintering on air. The effect of ultrasound treatment during the compaction process on density and microstructure of sintered ceramic has been studied.

Sintering condition was determined (Ultrasonic pressing at 400 MPa, sintering temperature - 1650 °C, isothermal exposure - 8 hours), which allows obtaining ceramics based on Ce: YAG with density about 100%, an average grain size - 4.57 µm and an average residual pore size - 0.94 µm.

It was found that the applied of ultrasonic treatment intensifies the process of grain growth, and in the case of manufacturing of ceramics in modes other than optimal it can lead to a decrease in density, the appearance and increase in the quantitative content of intragranular pores.

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References

- [1] Lukin E S 1997 Modern high-density oxide ceramics with controlled microstructures. Part VI. Production of optically transparent oxide ceramic materials *Refractories and Industrial Ceramics* **7** 4-10
- [2] Wang S F, Zhang J, Luo D W, Gu F, Tang D Y, Dong Z L, Tan G E B, Que W X, Zhang T S, Li S, Kong L B 2013 Transparent ceramics: processing, materials and applications *Progress in Solid State Chemistry* **41** 20-54
- [3] Tang Y, Zhou S, Yi X, Hao D, Shao X, Chen J 2018 The characterization of Ce/Pr-doped YAG phosphor ceramic for the white LEDs *Journal of Alloys and Compounds* **745** 84-89
- [4] Varney C R, Reda S M, Mackay D T, Rowe M C, Selim F A 2011 Strong visible and near infrared luminescence in undoped YAG single crystals *AIP Advances* **1.4** 042170
- [5] Mihokova E, Nikl M, Mares J A, Beitlerova A, Vedda A, Nejezchleb K, Blazer K, D'Ambrosio C 2007 Luminescence and scintillation properties of YAG: Ce single crystal and optical ceramics *Journal of luminescence* **126** 77-80
- [6] Singh G, Thomas V, Tiwari V S, Karnal A K 2017 Effect of cerium doping on optical and scintillation properties of transparent YAG ceramic *Ceramics International* **43** 9032-9040
- [7] Dong J, Shirakawa A, Ueda K 2006 Efficient Yb³⁺: Y₃Al₅O₁₂ ceramic microchip lasers 2018 *Applied physics letters* **89** 091114

- [8] Valiev D, Han T, Stepanov S, Vaganov V and Paygin V 2018 The effect of BaF₂ concentration and particle size distribution on the luminescence efficiency of YAG: Ce³⁺ phosphors *Materials Research Express* **5** 096201
- [9] Xia Z, and Andries M 2017 Ce³⁺-Doped garnet phosphors: composition modification, luminescence properties and applications *Chemical Society Reviews* **46** 275-299
- [10] Chen D and Yan C 2014 Transparent Ce³⁺:Y₃Al₅O₁₂ glass ceramic for organic-resin-free white-light-emitting diodes *Ceramics International* **40** 15325-15329
- [11] Osipov V V, Ishchenko A V, Shitov V A, Maksimov R N, Lukyashin K E, Platonov V V, Orlov A N, Osipov S N, Yagodin V V, Viktorov L V, Shulgin B V 2017 Fabrication, optical and scintillation properties of transparent YAG: Ce ceramics *Optical Materials* **71** 98-102
- [12] Dvilis E S, Khasanov O L, Sokolov V M, Pokholkov Y P Method for compacting powder materials into articles and a mold for implementing the method *U.S. Patent No. 6919041 B2* 19 Jul. 2005
- [13] Dvilis E S 2013 Regularities of the consolidation processes of powder systems at variable deformation and physical influences conditions Doctoral dissertation (In russian).
- [14] Dvilis E S, Khasanov O L, Sokolov V M 2016 The relationship between the parameters of the state of pressing powder and properties of ceramics sintered from it *Fundamental Research* **11** 691-697