

Influence of Ca and Mg doping on the microstructure and optical properties of YAG ceramics

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Ceramics of yttrium aluminum garnet doped with Ca or Mg are produced by solid state reaction under vacuum sintering. The influence of CaO and MgO additives themselves on microstructure and optical properties of YAG ceramics is investigated. Ceramics of Mg-doped YAG is transparent while ceramics of Ca-doped YAG is fully opaque due to high concentration of residual porosity into later. Changing concentration of Ca affects significantly on the grain growth, the average grain size increase with increasing of Ca concentration. Changing concentration of Mg from 0.05 to 0.5 at.% doesn't influence on grain size of the ceramics. It is proposed that liquid appears on the grain boundaries of the ceramics due to CaO additive. This liquid causes increasing the diffusion of components through the grain boundaries that speed up the grain growth and traps the pores while no such liquid exists for MgO additive. This difference is determined by the different ways of interaction of CaO and MgO with the basic YAG components Al_2O_3 and Y_2O_3 . It is determined that the Mg concentration ranges in vicinity of 0.15 at.% Mg to produce Mg:YAG ceramics of higher transparency.

Keywords: Yttrium aluminum garnet ceramics, CaO additive, MgO additive, solid state reaction, vacuum sintering, microstructure, transparency.

Получена керамика иттрий алюминиевого граната (ИАГ), допированного ионами Ca и Mg, путем твердофазного синтеза при спекании в вакууме. Исследовано влияние добавок CaO и MgO на микроструктуру и оптические свойства керамики ИАГ. Керамика ИАГ допированная Mg, была прозрачной, в то время как керамика допированная Ca, полностью светонепроницаемая вследствие высокой остаточной пористости. Установлено, что изменение концентрации Ca от 0.16 до 0.5 ат.% значительно влияет на рост зерен в керамике, средний размер зерна увеличивается при увеличении концентрации Ca, а изменение концентрации Mg от 0,05 до 0,5 ат.% не влияет на размер зерен керамики. Предполагается, что жидкость, которая возникает на границах зерен керамики в случае применения добавки CaO, способствует диффузии компонент через межзерненную границу, вызывая повышение скорости роста зерна и захват пор. В то же время при допировании ИАГ магнием жидкость на межзерненной границе не возникает. Такое отличие определяется разными путями взаимодействия CaO и MgO с основными компонентами керамики ИАГ — Al_2O_3 и Y_2O_3 .

Вплив допування Ca та Mg на мікроструктуру і оптичні властивості кераміки ІАГ. *М.А.Чайка, О.М.Вовк, А.Г.Дорошенко, В.К.Клочков, П.В.Матейченко, С.В.Пархоменко, А.Г.Федоров.*

Одержано кераміку ітрій алюмінієвого гранату (ІАГ), що допований іонами Ca та Mg, шляхом твердофазного синтезу при спіканні у вакуумі. Досліджено вплив добавок

CaO та MgO на мікроструктуру та оптичні властивості кераміки ІАГ. Кераміка ІАГ, що допована Mg, прозора в той час як кераміка, що допована Ca, була повністю світлоне-прозора внаслідок високої залишкової пористості. Встановлено, що зміна концентрації Ca у межах 0.16–0.5 ат.% значно впливає на ріст зерен у кераміці, середній розмір зерна збільшується зі збільшенням концентрації Ca, а зміна концентрації Mg від 0.05 до 0.5 ат.% не впливає на розмір зерен кераміки. Припущено, що рідина, яка виникає на границях зерен кераміки у випадку застосування добавки CaO, сприяє дифузії компонент через міжзернову границю і таким чином спричиняє підвищення швидкості росту зерна і захоплення пор. В той же час при допуванні ІАГ магнієм рідина на міжзернені границі не виникає. Така відмінність визначається різними шляхами взаємодії CaO і MgO з основними компонентами кераміки ІАГ — Al_2O_3 і Y_2O_3 . Встановлено, що для одержання кераміки, що допована Mg, з найвищою прозорістю необхідна концентрація близько 0.15 ат.% Mg.

1. Introduction

Over the past decade, solid-state lasers have demonstrated remarkable power in scaling [1–3]. Largely, the emergence of solid-state lasers as competitive high-power devices is due to the availability of highly efficient (60 percent), high-power (> 100 W), low-cost ($< \$10/\text{W}$) laser diode bars [4].

Cubic structure materials like yttrium aluminum garnet (YAG) now can be fabricated as ceramics with optical uniformity that is better than found in YAG crystals (for both dopant uniformity and variations in index of refraction), with scattering loss coefficients comparable to the YAG crystals (< 0.15 %/cm) [5, 6]. These materials can be also produced in sizes that the YAG crystals cannot achieve (e.g., 400×400 mm² slabs) [6].

In recent years tetrahedral coordinated Cr⁴⁺-doped YAG attracted a great deal of attention due to its potential use as tunable solid state lasers in the spectral range of 1.35–1.55 μm [7] or as passive Q-switcher for laser systems based on YAG doped with rare earth ions such as Nd and Yb [8].

Existence of the tetravalent Cr in the crystal requires containing divalent additives such as Ca or Mg to compensate the difference in charge. Sugimoto et al. [9] have shown that considerable excess of the Ca²⁺ ions up to 6 times against Cr is needed to obtain optimal concentration of Cr⁴⁺ in the single crystal of Cr⁴⁺:YAG.

Traditionally sintering aids of SiO₂ are used in YAG ceramic technology to obtain the high transparent ceramics [10, 11]. For example, Ikesue and Kamata [12] have found that SiO₂ addition is crucial for achieving the completed phase formation of Nd:YAG ceramics with high density. But in the case of Cr⁴⁺:YAG ceramics the presence of SiO₂ decreases concentration of Cr⁴⁺ [13, 14]. Si⁴⁺ ions incorporated into YAG consume Ca²⁺ or Mg²⁺ that eliminates these

ions from the process of formation of Cr⁴⁺. Therefore the sintering aids of SiO₂ cannot be applied to create the transparent ceramics of Cr⁴⁺:YAG.

Two basic problems should be overcome for obtaining the high quality transparent Cr⁴⁺:YAG ceramics by solid state sintering reaction. First one the reaching of the high concentration of Cr⁴⁺ can be solved by introducing in ceramics an excess of divalent ions like Ca²⁺ or Mg²⁺ for charge compensation. But in contrast to the YAG single crystals in ceramics the extra phases contained of Ca or Mg can be released on the grain boundaries. The second problem deals with obtaining the high quality transparent ceramics of YAG without SiO₂ as sintering aids that challenges investigation of the sintering YAG ceramics without addition of SiO₂. Obviously a usage of CaO or MgO themselves as new sintering aids have to be checked.

These problems cannot be solved without knowledge about effects of CaO or MgO additives on micro-structure of the YAG ceramics. Many papers report about influence of CaO or MgO on YAG ceramic properties but in complex with other additives and no themselves. This paper deals with the investigation of influence of CaO and MgO themselves on micro-structure and optical properties of the YAG ceramics.

2. Experimental

Two series of YAG ceramics with CaO and MgO additives were sintered according to the protocol reported in [15]. High purity Al₂O₃ (purity > 99.99 %, Baikowski, $d = 0.15$ – 0.3 μm), Y₂O₃ (purity > 99.999 %, Alfa Aesar, $d \leq 10$ m), MgO (purity > 99.99 %, Alfa Aesar, $d > 0.1$ μm), CaO (purity > 99.999 %, Sigma Aldrich, $d \leq 0.1$ μm) were used as starting materials. Powders were taken in stoichiometric ratio of YAG, concentrations of Ca and Mg were

calculated according to replace of Y. The powder mixtures were homogenized in a ball mill for 15 h using high purity Al_2O_3 balls. The resulted slurry was dried for 1 day in air and was sieved through the 200-mesh screen to produce powder. The powder was uniaxial pressed at $P = 250$ MPa to obtain green bodies. The green bodies were heated in a vacuum furnace with gradual rise of temperature to 1750°C and soaking for 10 h to carry out solid state reactions and sintering for producing ceramics. First series of YAG ceramics prepared from powders contained 0.5, 0.25, and 0.16 at.% Ca are denoted as $\text{Ca} = 0.5$, $\text{Ca} = 0.25$ and $\text{Ca} = 0.16$, respectively. Another series of the YAG ceramics synthesized from powders with 0.5, 0.15, and 0.05 at.% Mg are denoted as $\text{Mg} = 0.5$, $\text{Mg} = 0.15$ and $\text{Mg} = 0.05$, respectively.

Optical investigation was performed with UV/Vis spectrophotometer Analytik Jena Specord 200, before optical measurements the ceramics surface was polished by diamond abrasive with gradual decreasing the size of the abrasive from 30 to 7 μm . After processing the ceramics had the shape of tablets with a diameter of 8 mm and a thickness of 1.2 mm.

The ceramics micro-structure was investigated by means of Scanning Electron Microscopy (SEM) JEOL JSM-6390LV, element analysis was performed by energy-dispersive X-ray spectroscopy (EDS) with Silicon Drift Detector (SDD) X-MaxN Oxford Instruments.

Dilatometric analysis (DLA) of the powders was performed with differential dilatometer Netzsch 402ED (Netzsch-Gerätebau GmbH, Germany) within 20 – 1500°C range in air. The heating rate was $10^\circ\text{C min}^{-1}$ and $\alpha\text{-Al}_2\text{O}_3$ was used as a reference. The compacts of special shape were prepared to carried out the DLA measurements.

3. Results

3.1. Shrinkage of Ca:YAG and Mg:YAG powders

Shrinkage of the compacts prepared from powders of $\text{Ca} = 0.5$ ($2.985 \text{ Y}_2\text{O}_3$, 0.015 CaO , $5 \text{ Al}_2\text{O}_3$) and $\text{Mg} = 0.5$ ($2.985 \text{ Y}_2\text{O}_3$, 0.015 MgO , $5 \text{ Al}_2\text{O}_3$) were investigated by means of dilatometric analysis up to 1470°C (see Fig. 1). At the range of 1000 – 1330°C (denoted as A) the rate of densification is almost equivalent for both powders. At temperature above 1330°C (denoted as B) the powder with $\text{Ca} = 0.5$ have lower rate of densification.

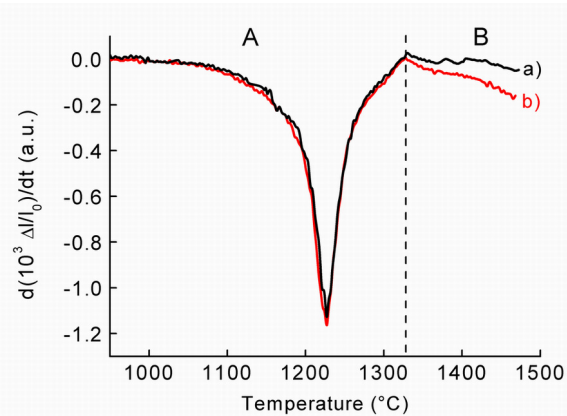


Fig. 1. Shrinkage rate of the powders: a) $\text{Ca} = 0.5$ and b) $\text{Mg} = 0.5$.

The shrinkage rate of these powders is superposition of two processes: 1) shrinkage due to different density of intermediate crystal phases formed under the solid state reactions of YAG synthesis and 2) sintering of the powders. The solid state reactions basically occur in A temperature range, while in B range the shrinkage determined by sintering. The identity of the shrinkage rates for both powders in the range A points to the same effect or absence of the effect of CaO and MgO additives on the rates of the intermediate solid state reactions occurred during the YAG synthesis. The different shrinkage rate of powders in the range B indicates different influence of the CaO and MgO additives on the powder sintering, which likely will affect on the properties of the ceramics prepared from these powders.

3.2. Ceramics of Ca:YAG

Ceramics of Ca:YAG was fabricated by means of the solid state reactions under vacuum sintering. Obtained samples of ceramics were totally opaque even after polishing. The ceramics surface was etched thermally at 1400°C for 15 h in air to reveal the grain boundaries. SEM images of the microstructure of Ca:YAG ceramics are presented in Fig. 2. The surface investigation shows that all samples of the ceramics Ca:YAG contain large amount of residual porosity. No deviation from the YAG stoichiometry was observed on the sample surfaces by EDS analysis that can pointed to absence of inclusions of secondary phases in the sample.

Fig. 3 shows the grain size distribution calculated by the linear intercept method [16] according equation Eq. 1 at least 350 grains are taken for each measurement.

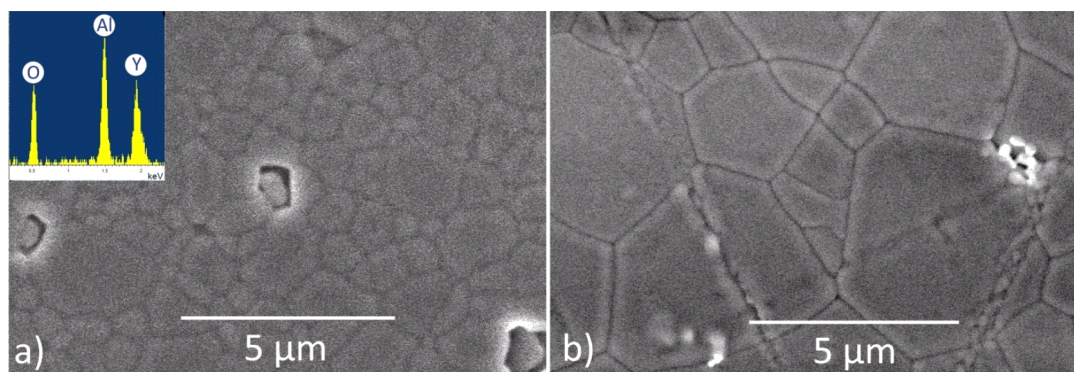


Fig. 2. SEM images of the thermally etched surface of ceramics samples: a) Ca = 0.16 and b) Ca = 0.5. Insert shows EDS spectrum of sample of Ca = 0.16.

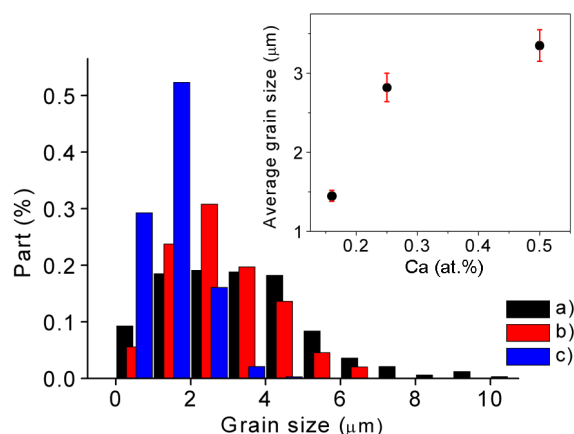


Fig. 3. Grain size distribution in ceramics samples: a) Ca = 0.5, b) Ca = 0.25, and c) Ca = 0.16. Insert shows dependences of the average grain size on concentration of Ca into ceramics of Ca:YAG.

$$G = \frac{1.56 \cdot L}{M}, \quad (1)$$

where G is the grain size, L is the length of a line that freely drawn on a high resolution SEM image and M indicates the magnification. The insert in Fig. 3 shows dependence of the average grain size on concentration of Ca into ceramics of Ca:YAG. The ceramics of Ca = 0.16, Ca = 0.25, and Ca = 0.5 have average grain size of $1.45 \pm 0.07 \mu\text{m}$, $2.8 \pm 0.2 \mu\text{m}$, and $3.4 \pm 0.2 \mu\text{m}$, respectively. Standard deviation was calculated using the Student's t-test. The rise of Ca concentration results in increase of the average grain size.

3.3. Ceramics of Mg:YAG

Ceramics of Mg:YAG was fabricated by means of the solid state reactions under vacuum sintering under the same conditions as the ceramics of Ca:YAG. X-ray diffrac-

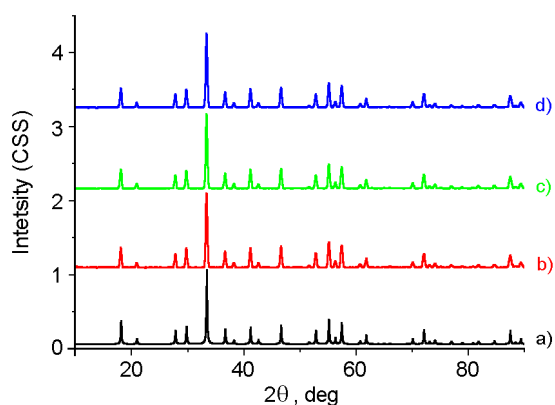


Fig. 4. XRD patterns of a) ICSD Card N170158 of YAG and Mg:YAG ceramics: b) Mg = 0.5, c) Mg = 0.15, d) Mg = 0.05.

tion patterns as-prepared samples shown in Fig. 4 are coincided with the crystal structure of the pure YAG phase corresponded to Inorganic Crystal Structure Database (ICSD) Card N 170158.

No new peaks or peak shifts are observed on the diffraction patterns of Mg:YAG ceramics comparing to the one of YAG. Related intensities of the diffraction peaks of all patterns presented in Fig. 4 are identical that means no preferred orientation of the ceramics grains of Mg:YAG takes place.

The SEM images of the surface microstructure of Mg:YAG ceramics are shown in Fig. 5. To reveal the grain boundaries the ceramics samples were etched at 1400°C for 15 h in air. The grain size distribution and average grain size don't depend on the concentration of Mg and consist of from 0.5 to 8 μm and $3.2 \pm 0.2 \mu\text{m}$, respectively.

The investigation of the sample surfaces revealed no porosity for whole range of Mg concentration. The EDS was applied to examine inclusions in these ceramics. No any

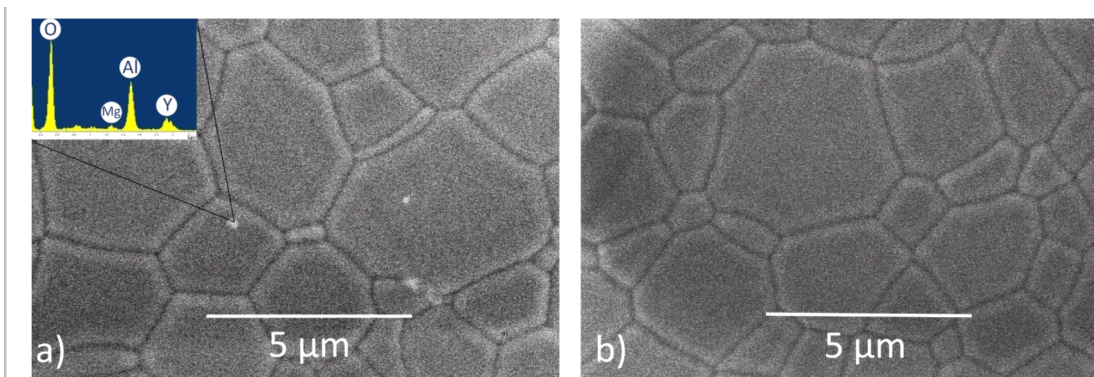


Fig. 5. SEM images of the surface after thermal etching of ceramics samples: a) Mg = 0.5; b) Mg = 0.05. Insert shows EDS spectrum from inclusion of impurity phase into sample Mg = 0.5.

inclusions were observed on a surface of the samples of Mg = 0.05 and Mg = 0.15 while the surface of the ceramic of MgO = 0.5 contained the inclusion of impurity phases richen with Mg and Al.

The sintered ceramics of Mg:YAG after polishing were investigated by means of optical absorption spectroscopy. Optical in-line transmittance spectra of Mg:YAG ceramics are shown in Fig. 6. The transmittance at 1064 nm, which is the most interest wavelength range, of the samples Mg = 0.5, Mg = 0.15, and Mg = 0.05 is 33, 79, and 73 % varies non monotonically. Increasing the concentration of Mg from 0.05 to 0.15 at.% increases the transmittance from 73 to 79 %, further increasing concentration of MgO drops the transmittance from 79 to 33 % probably due to the high scattering. The absorption band centered at 220 nm can originated from absorption of F center [17].

4. Discussions

CaO and MgO additives were applied as sintering aids to synthesize the YAG ceramics by the solid state reaction sintering in vacuum. The quite different effect of these additives on the optical quality of the YAG ceramics was revealed. The Mg:YAG ceramics was transparent while the Ca:YAG one was fully opaque. Obviously that such distinction appeared under ceramics synthesis, which consisted of the solid state reactions between the original oxide powders at range of 1000–1400°C and sintering the YAG grains formed in result of these reactions. In accordance with DLA (see Fig. 1) no difference in shrinkage behavior of the samples with both sorts of additives are observed in temperature range of the solid state reactions. Therefore it could be assumed that influence of the additives on the

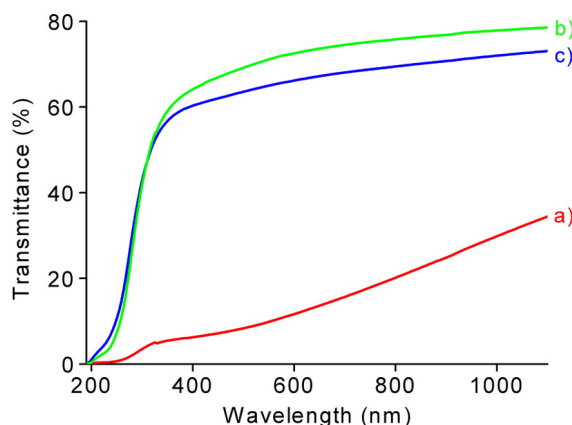


Fig. 6. Optical in-line transmittance spectra of mirror polished samples: a) Mg = 0.5, b) Mg = 0.15, and c) Mg = 0.05.

optical properties of the ceramics is caused by their different affecting on the YAG ceramics sintering of.

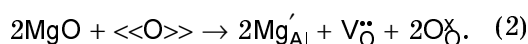
As has been shown (see Fig. 2, 3) the addition of CaO into the YAG ceramics affects the grain growth that leads to increase of the average grain size with increasing the concentration of CaO into Ca:YAG ceramics. The initial powders and sintering conditions were equal for all samples only Ca concentration was changed. It means that major factor of the change of the grain size distribution into the ceramic is an interaction between CaO and the basic components (Al_2O_3 or Y_2O_3). The phase diagram of the ternary system of Al_2O_3 – Y_2O_3 –CaO contains eutectic points at 1375 and 1395°C [18] as well as binary system of Al_2O_3 –CaO system has eutectic point at 1360°C [19] that can cause formation of the liquid on the grain boundaries under the sintering. Such liquid increases the diffusion of the components through the grain boundaries that speeds up the grain growth and traps the

pores. The high concentration of pores in Ca:YAG ceramics brings adverse effects on the optical properties. Even a small concentration of CaO leads to formation of the totally opaque ceramics.

In contrast with Ca:YAG ceramics it was shown that the ceramics of Mg:YAG is transparent. The dependence of Mg:YAG ceramics transparency from Mg concentration is non monotonic. The in-line transmittance rises from 73 to 79 % with increasing the concentration of Mg dopant from 0.05 to 0.15 at.% and further dropping to 33 % at 0.5 at.% of Mg.

Such a behavior agrees with the phase diagram of the ternary systems of Al_2O_3 – Y_2O_3 – MgO [20]. No liquid phases exist under the sintering conditions of Mg:YAG, only the set of solid solutions of MgO in Al_2O_3 or Y_2O_3 are found on the binary phase diagrams [21, 22]. The change of MgO concentration doesn't significant affect on the grain size distribution of Mg:YAG ceramic. At 0.5 at.% of Mg the Mg-contained phases precipitate as island but don't distribute along the grain boundaries (see Fig. 5).

Our data also agree with Yang et al. [23] who suggested that effect of MgO resulted in the solid solution formation by substitution of Al^{3+} by Mg^{2+} as follows Eq. 2.



According to Eq. 2, one expects that the formation of oxygen vacancies improves the volume diffusion coefficient and can support the vacancy diffusion from the pore to the grain boundaries. The vacancies are eliminated at the grain boundaries causing the enhanced densification rate, which can be observed on the shrinkage curve (b) of Fig. 1. In the case of relatively low concentration of MgO this mechanism allows to obtain well transparent ceramics. But increasing the level of MgO doping causes lowering transparency resulted in the light scattering on the precipitates of Mg contained phases.

Many authors [23–26] used magnesium oxide as the sintering aids to create the high transparent ceramics of YAG, but they have used wide range of amount MgO from 0.04 [24] to 0.5 wt.% [25]. In this paper we have shown that the optimal MgO concentration is about of 0.15 at.%.

4. Conclusions

Ceramics of Ca:YAG and Mg:YAG were produced by solid state reaction sintering under vacuum at 1750°C for 10 h. The influence of CaO and MgO additives on micro-

structure and optical properties of the YAG ceramics was investigated and the quite different effect were revealed. Ceramics of Mg:YAG is transparent while ceramics of Ca:YAG is fully opaque due to high concentration of residual porosity into the later one. Changing the concentration of Ca affects significantly on the grain growth, the increase of Ca concentration leads to increasing the average grain size. Changing the concentration of Mg from 0.05 to 0.5 at.% doesn't influence on the grain size of the ceramics. It was proposed that such different behavior is due to a liquid appears on the grain boundaries of the ceramics in Ca:YAG ceramics while there is no such liquid in Mg:YAG. This difference is determined by the different ways of interaction of CaO and MgO with the basic YAG components — Al_2O_3 and Y_2O_3 .

It was determined the concentration of Mg to produce Mg:YAG ceramics of the higher transparency ranges in vicinity of 0.15 at.% Mg.

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