

Mutual influence of additives of Ca and Si on properties of Cr-doped YAG ceramics

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Cr-doped yttrium aluminum garnet ceramics with different concentration of additives Ca and Si were synthesized by vacuum reaction sintering. It was established that simultaneous doping with Ca and Si effects crucially on morphology and optical ceramics properties. Average grain size of such ceramics can reach to $1.08 \pm 0.06 \mu\text{m}$ that is much more less against the ceramics without Ca dopant. The optical properties of the ceramics deteriorate significantly with increase of Ca concentration. The degree of Cr^{4+} transformation to Cr^{3+} under air annealing is not well due to competition between Cr^{4+} and Si^{4+} ions to be charge compensated by Ca^{2+} . Sintering aid SiO_2 , which used in widespread ceramic technology to produce the high optical quality ceramics based on YAG, cannot be applied to produce the Cr^{4+} -doped YAG ceramics with Ca as a charge compensator.

Keywords: Cr:YAG, ceramics, optical absorption, morphology, sintering aid.

Керамика иттрий алюминиевого граната (ИАГ), допированного ионами Cr и разной концентрацией добавок Ca и Si, получена методом твердофазного синтеза в вакууме. Установлено, что одновременное допирование Ca и Si критически влияет на морфологию и оптические свойства керамики. Средний размер зерна такой керамики может достигать $1.08 \pm 0.06 \mu\text{м}$, что намного меньше, чем в керамиках без применения Ca в качестве допанта. Оптические свойства керамики значительно ухудшаются при увеличении концентрации Ca. Степень преобразования Cr^{3+} в Cr^{4+} в условиях отжига на воздухе невысокая из-за конкуренции между ионами Cr^{4+} и Si^{4+} за ион компенсатор заряда Ca^{2+} . Установлено, что спекающая добавка SiO_2 , которая используется в широко распространенных технологиях получения керамик высокого оптического качества на основе ИАГ, не может быть применена для получения керамики ИАГ, допированной ионами Cr^{4+} с использованием Ca в качестве компенсатора заряда.

Взаємний вплив добавок Ca та Si на властивості кераміки ітрій алюмінієвого гранату, що допований іонами Cr. *М.А.Чайка, О.М.Вовк, Н.А.Сафронова, С.В.Пархоменко, А.Г.Дорошенко, О.В.Толмачов.*

Кераміка ітрій алюмінієвого гранату (ІАГ), що допований іонами Cr та різною концентрацією добавок Ca та Si, одержано методом твердофазного синтезу у вакуумі. Встановлено, що одночасне допування Ca та Si критично впливає на морфологію та оптичні властивості кераміки. Середній розмір зерна такої кераміки може досягати $1.08 \pm 0.06 \mu\text{м}$, що набагато менше, ніж у кераміках без використання Ca як допantu. Оптичні властивості кераміки значно погіршуються з підвищенням концентрації Ca. Ступінь перетворення Cr^{3+} в Cr^{4+} в умовах відпалу на повітрі є невисоким завдяки конкуренції між іонами Cr^{4+} та Si^{4+} за іон компенсатор заряду Ca^{2+} . Встановлено, що спікаюча добавка SiO_2 , яка широко використовується у керамічних технологіях для одержання керамік високої оптичної якості на основі ІАГ, не може бути застосована для одержання кераміки ІАГ, що допований іонами Cr^{4+} при використанні Ca як компенсатора заряду.

1. Introduction

Cr⁴⁺-doped yttrium aluminum garnet (Cr⁴⁺:YAG) attracts interest due to unique characteristics of being both a saturated absorber for 1.06 μm laser emission of Nd:YAG [1, 2] and tunable mid-IR laser in the spectral range of ≈ 1.3 to 1.6 μm with significant practical applications [3, 4].

Garnet crystals (Y₃Al₅O₁₂) are cubic and belong to Ia-3d space group. They have stoichiometric formula [C₃][A₂][D₃]O₁₂, where "C", "A", and "D" represent dodecahedrally, octahedrally, and tetrahedrally coordinated sites, respectively. "A" and "D" sites are occupied with Al ions while "C" is occupied with Y ions. The YAG crystals incorporate Cr only in the form of Cr³⁺ into "A" site when Cr is one dopant [5]. Ionic radius of Cr³⁺ ($r = 0.062$ nm) [5] is not differ significantly from radius of Al ions in "A" site ($r = 0.053$ nm) but it is too large in compare with radius of Al ions in "D" site ($r = 0.039$ nm) [6], for occupying tetrahedral coordinated site "D" with Cr³⁺. Appearing tetravalent Cr ions in YAG crystal lattice requires occurrence charge compensators like divalent additives of Ca or Mg. These additives occupy "C" site while Cr⁴⁺ ions take up the both "A" and "D" sites. The Cr⁴⁺ ions can be obtained by annealing the Cr:YAG under oxidative conditions. Portion of oxidized Cr ions and ratio between Cr⁴⁺ in "A" and "D" positions are influenced by many factors like temperature and time of annealing, concentration of charge compensators, oxidative potential of environment, presence other tetravalent cations in the crystal lattice etc.

Laser ceramic possesses several advantages in compare with single crystal, for example, easy and less expensive process of fabrication, ability to produce large size elements with high concentration of activator, preparation of multilayer and multi-functional ceramic structures etc. [7].

Ikesue et al. [8] first reported highly efficient laser gain of transparent Nd:YAG ceramics produced by sintering a powdered mixture of Al₂O₃, Y₂O₃, and Nd₂O₃ at 1750°C for 8 h. They found that addition of 0.14 wt. % (1.35 mol. %) SiO₂ was crucial for sintering Nd:YAG to transparency. This phenomenon has been confirmed later [9] and now SiO₂ of different concentration is commonly used as sintering aid to produce the Nd:YAG ceramics of laser quality.

Production of Cr⁴⁺:YAG ceramics under the same technological process as Nd:YAG is

very attractive for developing the multilayer structures consisted on active gain and passive Q-switcher, which based on the microchip laser elements can be created.

But in the case of producing the Cr⁴⁺:YAG ceramics some effects concerned SiO₂ can occur. The first one is the enhanced solubility of SiO₂ in YAG due to presence of Ca [10], which can deplete concentration of Si ions on the grain boundaries or can combine Si⁴⁺ ions dissolved in the YAG crystal lattice with Ca²⁺ ions that cause crucial change of concentration of Si species taken part in the sintering processes. The second effect of SiO₂ is the competition between Si⁴⁺ ions and Cr⁴⁺ ions to be charge compensated by Ca²⁺ that can to occasion the lack of Cr⁴⁺ in the Cr:YAG ceramics [11].

Until now, there are few reports dealt with a systematic study of influence of SiO₂ and CaO on the properties of the Cr:YAG ceramics [11, 12]. In 1996 Ikesue [12] first reported the possibility of creation the Cr⁴⁺:YAG ceramics. They investigated the influence of ambient environment on Cr charge state. The ceramics Cr:YAG sintering under vacuum has better transparency but didn't contain Cr⁴⁺ in compare with the sample sintering under vacuum. Zhou et al. [11] reported that a presence of Si⁴⁺ decreased concentration of Cr⁴⁺ but they didn't explain the reason of such effect.

This article deals with study of influence of divalent dopant of Ca²⁺ on the optical properties as well as the microstructure evolution of Cr:YAG ceramics prepared by conventional ceramics techniques of solid state reaction under vacuum sintering with applying of SiO₂ as a sintering aid. The second problem to be investigated is the effect of SiO₂ additive on the efficiency of appearing the Cr⁴⁺ ions in the Cr:YAG ceramics with Ca²⁺ as a charge compensator.

2. Experimental

High purity oxide powders of Al₂O₃ (purity >99.99 %, Baikowski), Y₂O₃ (purity >99.999 %, Alfa Aesar), Cr₂O₃ (purity >99.9 %, Alfa Aesar), CaO (purity >99.9, Sigma Aldrich) were used to produce ceramics. Tetraethoxysilane (TEOS, 99.999 %, Sigma-Aldrich, USA) (0.9 mol. %) was used for sintering aid. Powders taken in stoichiometric ratio of YAG were homogenized in a ball mill for 15 h with high purity Al₂O₃ balls in isopropyl alcohol. The slurry was overnight dried in air at 70°C

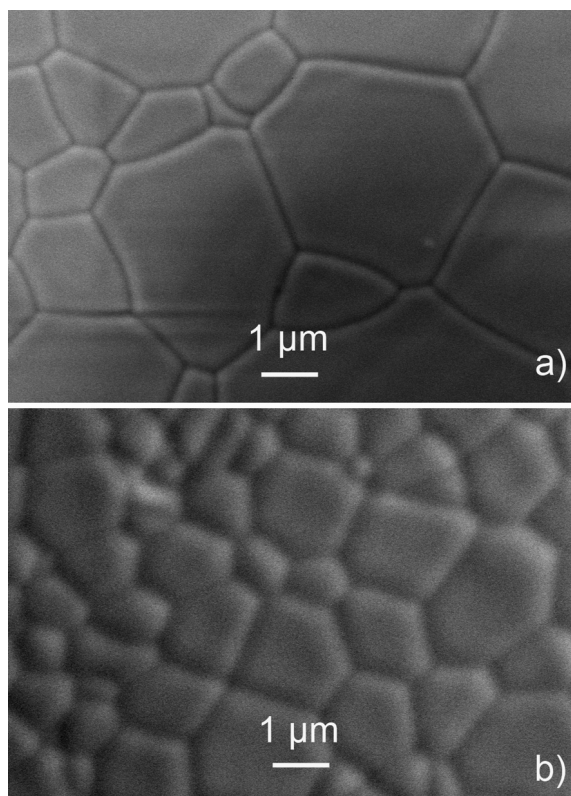


Fig. 1. SEM surface images of Cr:YAG ceramics with a) 0.87 and b) 1.75 at.% Ca.

and was sieved through a 200-mesh screen. The compacts were prepared by uniaxial pressing at $P = 250$ MPa and were annealed in air for 4 h at 800°C before vacuum sintering at 1750°C for 10 h. Cr:YAG ceramics with Cr concentration of 0.35 at.% and Ca concentration of 0.87 and 1.75 at.% was obtained by solid state reactions under vacuum sintering. Ceramics surface was polished with diamond abrasive by gradually decreasing the size of the abrasive from 30 to 7 μm for optical investigation. The samples of Cr:YAG ceramics of cylindrical shape with a diameter of 8 mm and a thickness of 1.2 mm were resulted in. Air annealing at 1400°C for 10 h was performed after vacuum sintering for recharging Cr^{3+} to tetra-valent state.

Morphology of the ceramics was investigated with Scanning Electron Microscopy (SEM) JEOL JSM-6390LV. Optical investigation was carried out with UV/Vis spectrophotometer PerkinElmer Lambda-35 in the range of 190–1100 nm.

3. Results and discussions

The YAG ceramics doped with Cr, Si, and Ca was fabricated by means the solid-state reactions under vacuum sintering. Influence

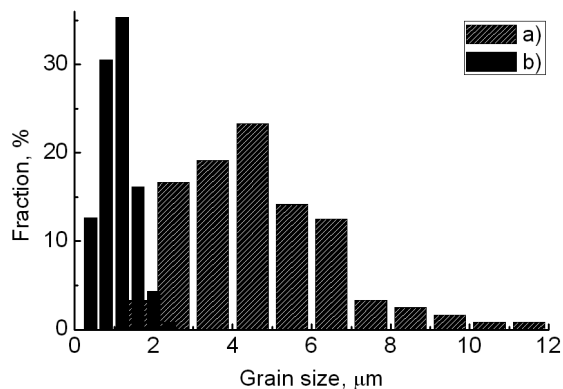


Fig. 2. Grain size distribution of Cr:YAG ceramics with a) 0.87 and b) 1.75 at.% Ca.

of Ca concentration on the microstructure and optical properties of Cr:YAG were investigated. Choice of the dopant concentration based on the following: the concentration of SiO_2 (0.9 mol.%) was taken as conventional used for producing the high quality Nd:YAG ceramics [6, 8, 9], the Cr amount (0.35 at.%) based on the maxima of the optimal concentration that we known from the literature [13], the Ca concentration was limited up by emergence of the phases contained of Ca. Finally, the YAG ceramics doped by Ca, Cr, Si were obtained with 0.87 at.% of Ca and atomic ratio of $\text{Ca}:\text{Cr}:\text{Si} = 3:1:2$ (**sample 1**) and with 1.75 at.% of Ca which corresponds $\text{Ca}:\text{Cr}:\text{Si} = 6:1:2$ (**sample 2**).

The SEM images of the microstructure of **sample 1** and **sample 2** of the Cr:YAG ceramics are presented in Fig. 1a and Fig. 1b, respectively. To reveal the grain boundaries the ceramics were etching at 1300°C for 15 h in air. The presence of the secondary phases as inclusions was not observed on the surface of the both samples. This indicates that Ca and Si under taken concentration were dissolved completely into the Cr:YAG ceramics.

Fig. 2 shows grain size distribution of the Cr:YAG ceramics with different Ca concentration. Calculation of the grain size distribution was carried out with linear-except method, which in standard deviation was calculated with the Student s-test. The ceramics with 0.87 at.% Ca in compare with one of 1.75 at.% has large average grain size and wider grain size distribution 4.8 ± 0.4 μm and 1.08 ± 0.06 μm , respectively. The ceramics Nd:YAG obtained under this technology but without Ca possess much higher average grain size around 10 μm [14]. The presence of Ca into the

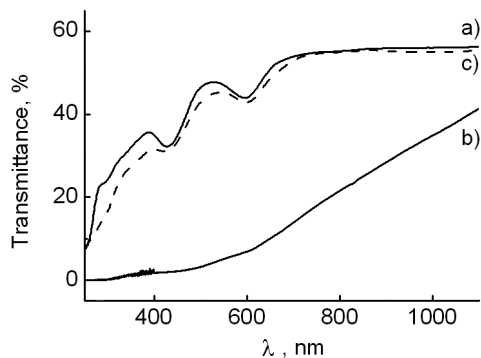


Fig. 3. Transmission spectra of Cr:YAG ceramics after vacuum sintering with a) 0.87 and b) 1.75 at.% Ca and after air annealing at 1400°C for 10 h c) 0.87 at.% Ca (dash line).

Cr:YAG ceramics inhibits grain growth resulted in much smaller average grain size of this ceramics in compare with the Ca-undoped YAG ceramics. Decrease of the average grain size with increasing the Ca concentration points out on significant effect of the Ca dopant on the ceramics microstructure.

The Cr:YAG ceramics with different concentration of Ca were investigated with the optical absorption spectroscopy. Fig. 3 (a, b) shows the optical transmission spectra of the Cr:YAG ceramics with Ca concentration of 0.87 and 1.75 at.% after vacuum sintering. In-line transmittance of 57 and 40 % at 1064 nm were observed for the samples with Ca contents of 0.87 and 1.75 at.%, respectively. Ca additive affects drastically on optical absorption of the Cr:YAG ceramics. Two broad absorption bands at ≈ 590 and 430 nm corresponded to ${}^4A_2 \rightarrow 4T_2$ and ${}^4A_2 \rightarrow 4T_1$ transition in Cr^{3+} ion are presented in the spectra of the sample with lower Ca concentration giving the characteristic bright green color of the Cr:YAG ceramics sintering under vacuum. These bands are overlapped with strong scattering in the transmission spectrum of the samples with the higher Ca concentration. Generally it can be seen that the optical properties of ceramics depended crucially on concentration of Ca whose increasing raises deterioration of the ceramics optical properties.

The Cr:YAG ceramics to be apply as Q-switcher or tunable laser elements must contain tetravalent Cr in the tetrahedral coordinated sites of the YAG crystal lattice. After vacuum sintering such ceramics con-

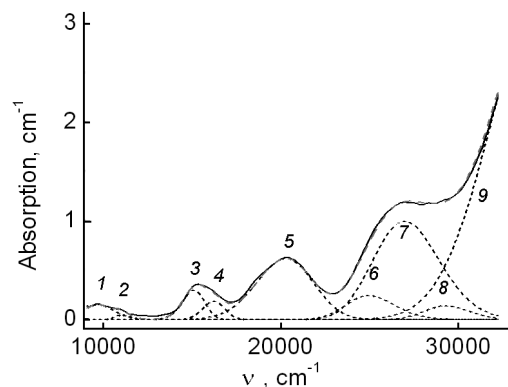


Fig. 4. Difference between spectra of Cr:YAG ceramics (0.87 at.% Ca) after vacuum sintering and after air annealing at 1400°C for 10 h resolved into nine modified Lorentzian peaks. Fitted curve is shown by dash red line.

tains only trivalent Cr in octahedral position therefore recharging Cr from trivalent to tetravalent state is needed that usually provided by air annealing.

Fig. 3c shows the transmission spectra of **sample 1** (0.87 at.% Ca) after air annealing at 1400°C for 10 h. The minor change in the spectra was observed. Fig. 4 shows the difference of absorption before and after annealing of **sample 1** that consists on numbers of absorption bands that assignment according the literature data are presented in Table. The absorption bands corresponded to Cr^{4+} ions that occupy both octahedral "A" and tetrahedral "D" sites in the crystal lattice were revealed. The absorption at 1064 nm looks too slight to be used for Q switching.

The following way of the affect of simultaneous doping with Ca and Si of the Cr:YAG ceramics can be proposed based on results obtained. Kuklja et al. [16] proposed that Si^{4+} incorporation in the YAG crystal lattice as well as in other crystal lattice of origin and intermediate phases taken part in the YAG ceramics synthesis introduces extra positive charge. To compensate this charge the cation vacancies should be generated. Stevenson et al. [9] suggested that the cation vacancies into YAG appeared due to Si^{4+} doping increase ion diffusivity of Y and Al that caused increasing the ceramics densification in compare with Si-undoped YAG. In our case, when Ca^{2+} ion is introduced into the YAG crystal lattice, the neutral complex of $[Ca^{2+}...Si^{4+}]$ is formed and the cation vacancies don't emerge. The lack of cation vacancies causes the deterioration of

Table. Characteristics of absorption bands in the difference between spectra of Cr:YAG ceramics (0.87 at.% Ca) after vacuum sintering and after air annealing at 1400°C for 10 h: assignment, peak position ν_p and λ_p , width $\Delta\nu_{FWHM}$

No.	ref.	Ions	Assignment	Lattice position	ν_p , nm	λ_p , cm ⁻¹	$\Delta\nu_{FWHM}$, cm ⁻¹
1	[5]	Cr ⁴⁺	${}^3B_1({}^3A_2) \rightarrow {}^3A_2({}^3T_1)$	Tetrahedral site	1032	9691	2004
2	[5]	Cr ⁴⁺	${}^3B_1({}^3A_2) \rightarrow {}^3E({}^3T_2)$	Tetrahedral site	906	11042	964
3	[5]	Cr ⁴⁺	${}^3B_1({}^3A_2) \rightarrow {}^3E({}^3T_1)$	Tetrahedral site	662	15105	1494
4	[5]	Cr ⁴⁺	${}^3B_1({}^3A_2) \rightarrow {}^3E({}^3T_1)$	Tetrahedral site	617	16216	1449
5	[5]	Cr ⁴⁺	${}^3B_1({}^3A_2) \rightarrow {}^3E({}^3T_1)$	Octahedral site	493	20275	3764
6	[5]	Cr ⁴⁺	Not assigned	Octahedral site	400	24969	3246
7	[15]	F ⁺	Unknown	Oxygen vacancy	342	29282	3010
8	[5]	Cr ⁴⁺	Not assigned	Octahedral site	371	26968	4381
9	[5]	Cr ⁴⁺	${}^3T_1 \rightarrow {}^3T_1$	Octahedral site	283	35354	8077

the ceramics densification followed by worsening it optical quality.

Solubility of Ca and Si ions in YAG is very low when they solute individually. It was reported that Ca solubility into YAG is 300–400 ppm [17], solubility limit of Si in YAG ranges between 600 ppm and 0.1 % [18]. But simultaneous doping of YAG with Ca and Si significantly increases solubility of the both two ions [10], that can be evidence of existence of [Ca²⁺...Si⁴⁺] complex. We assume that Si⁴⁺ mostly combines with Ca²⁺ when enough amounts of later is. Recharging Cr³⁺ to tetravalent state requires addition to the Cr:YAG ceramics a charge compensator like divalent ion of Ca. Based on assumption that one Ca atom can compensate one atom of Si or Cr the atomic ratio between Ca:Si:Cr was chosen as 3:2:1 (**sample 1**). But it was determined that degree of Cr³⁺ transformation to Cr⁴⁺ of such composition was too low to be applied. To our mind one of the reason of such a phenomenon could be the deficiency of Ca as charge compensator caused by its evaporation.

To check this hypothesis the amount of Ca in the ratio of Ca:Si:Cr = 6:2:1 (**sample 2**) was increased. But the optical properties of the ceramics obtained with this composition became worse significantly. It was translucent (Fig. 3b) that make unreasonable to measure Cr³⁺ transformation to Cr⁴⁺ on this sample. It points that fine tuning of Ca concentration is needed to obtain the Cr:YAG ceramics of high quality.

4. Conclusions

Simultaneous doping with Ca and Si of Cr:YAG ceramics crucially affects the optical and morphological ceramics properties. Ca and Si can form complex, which combines Si ions that inhibits generation of cation vacancies. The lacking cation vacancies results in decreased diffusion of Al and Y under the ceramics sintering and deterioration of the ceramics optical quality. Combining Ca²⁺ ions with Si⁴⁺ causes the lowering concentration of Cr⁴⁺ ions that can be formed under Cr³⁺ oxidation, due to the lack of charge compensator of extra charge of Cr⁴⁺. Increasing the concentration of Ca²⁺ ions causes the deterioration of the ceramics optical properties therefore cannot be applied to increase the Cr⁴⁺ concentration.

It should be concluded that sintering aid SiO₂, which is widely used in ceramic technology, cannot be applied in pair with Ca dopant to produce the high quality optical ceramics Cr:YAG.

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