

Investigation of distribution of metals in Cr³⁺-doped Y₃Ga₅O₁₂ and Gd₃Sc₂Ga₃O₁₂ using ICP-OES and EDX

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In this study the series of Cr³⁺-doped Y₃Ga₅O₁₂ (YGG) and Gd₃Sc₂Ga₃O₁₂ (GSGG) garnets were investigated. The garnet samples doped with a different amount of Cr³⁺ were synthesized using an aqueous sol–gel combustion synthesis method. The phase purity and morphology of the obtained garnets were characterized by X-ray diffraction (XRD) analysis and scanning electron microscopy (SEM). The chemical composition of differently Cr³⁺-doped garnet structure compounds was analysed and compared with the nominal one. The content of elements in all samples was determined by inductively coupled plasma optical emission spectrometry (ICP-OES) after dissolving these garnets in diluted nitric acid and by energy-dispersive X-ray spectroscopy (EDX) coupled with SEM. The empirical formula were calculated for both garnet series and compared with the theoretical formula.

Keywords: garnets, YGG, GSGG, sol–gel synthesis, elemental analysis, ICP-OES, EDX

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INTRODUCTION

Garnets are among the most important hosts for luminescent active centers, such as lanthanide and transition metal ions, and are useful for various optical applications due to a high thermal stability, hardness, optical isotropy and good

thermal conductivity, particularly for lasing and solid state lighting applications [1, 2]. They have a number of diverse technological applications. There are three main classes of synthetic garnets based on the atomic species at the octahedral and tetrahedral sites (aluminum, iron and gallium garnets) [3, 4].

The gallium garnets are also important host materials for laser technology. Among them, yttrium gallium

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garnet (YGG), gadolinium scandium gallium garnet (GSGG), gadolinium scandium aluminum garnet (GSAG) and gadolinium gallium garnet (GGG) are the most common [4]. GSGG is a member of the garnet family whose molecular formula is $Gd_3Sc_2Ga_3O_{12}$ [5]. GSGG has been widely used as the host for lasers, scintillators, optical recording media and the substrate material for thin films of high-temperature superconductors and laser host material [6, 7]. GSGG crystals are more resistant to radiation than the YAG crystals [8]. $Y_3Ga_5O_{12}$ (YGG) has many advantages for laser materials: stability, hardness, optical isotropy, having a good thermal conductivity (9 W/mK) [9, 10]. YGG is a promising candidate for applications that rely on long coherence lifetimes, such as optical quantum memories and photonic signal processing.

Rare-earth and transition metal ion-doped lanthanide gallium garnets have been found suitable for applications in the fields of biomedicine, display devices and have been widely used as superior laser host materials in many fields [11, 12]. In particular, GSGG and GSAG, when doped with Cr^{3+} and Nd^{3+} ions, have been shown to be promising host materials for the tunable infrared lasers [4, 12]. Cr^{3+} -doped GSGG is an excellent tunable laser crystal, in which Cr^{3+} can substitute Sc^{3+} in octahedral sites [5]. GSGG is supposed to be more than three times effective as a similar material containing aluminum. YGG doped with Cr^{3+} ions are the important laser materials used in the room temperature tunable lasers in the near-infrared spectral range. It has the potential application in the up conversion luminescence materials [13]. Moreover, Cr^{3+} -doped YGG are very important because of their potential application as high-temperature sensors [14]. In addition, these mixed-metal garnets are potential candidates for application as deep red light-emitting diodes, which could be used even for cultivation of plants and vegetables. The human eye sensitivity in the deep red range is very low, but radiation in this wavelength range has a rather high penetration depth into a biological matter. Therefore, the europium or chromium-doped garnets could also be applied in the new field as optical imaging [15].

Stoichiometry is a very important feature of mixed-metal oxides influencing or sometimes even determining the quality of physical properties of these compounds. Therefore, to know the real stoichiometry of metals in the multinary system is a very important task for materials scientists. Stoichiometry is a branch of chemistry that deals with the quantitative relationships that exist between the reactants and the products in chemical reactions. When elements are combined resulting in a chemical reaction, the outcome of the reaction can be predicted on the basis of the elements and quantities involved. However, the real stoichiometry of metals which react at the experimental conditions can be different from the nominal stoichiometry. In this work, a series of high quality Cr^{3+} -doped gadolinium scandium gallium (Cr:GSGG) and yttrium gallium (Cr:YGG) garnet powders with different concentration of Cr^{3+} -ions (3, 5, 8, 10, 12, 15 and 20 at.%) have

been synthesized by aqueous sol-gel combustion synthesis method. The chemical composition of different Cr-doped garnet structure compounds has been investigated and compared by two analytical techniques (ICP-OES and EDX) in this study.

EXPERIMENTAL

In the synthesis processing gallium oxide (Ga_2O_3 ; 99.99%; Alfa Aesar), gadolinium oxide (Gd_2O_3 ; 99.99%; Treibacher Industrie AG), scandium oxide (Sc_2O_3 ; 99.99%; Treibacher Industrie AG), yttrium oxide (Y_2O_3 ; 99.99%; Alfa Aesar), chromium (III) nitrate nonahydrate ($Cr(NO_3)_3 \cdot 9H_2O$; 99%; Sigma-Aldrich), tris-(hydroxymethyl)-aminomethane (TRIS; $NH_2C(CH_2OH)_3$; 99.9%; Carl Roth) and nitric acid (HNO_3 ; 65%; Reachem) were used as starting materials. For the ICP-OES analysis Gd, Sc, Ga, Y and Cr ICP single-element standard solutions (1000 mg/l, Roth) were used. All garnet samples were synthesized using a sol-gel combustion method [15, 16]. Firstly, the metal oxides were dissolved in boiling concentrated nitric acid. The acidity of these solutions was reduced by 3 times evaporating them and diluting with deionized water. Appropriate amounts of the prepared $M(NO_3)_3$ solutions in deionized water were mixed together (Gd^{3+} , Sc^{3+} , Ga^{3+} for GSGG and Y^{3+} , Ga^{3+} for YGG synthesis). Next, a necessary amount of the complexing agent TRIS was added to these solutions. The beaker was covered with watch glass and the solution was continuously mixed for 1 h using a magnetic stirrer at around 70 °C. After a transparent sol was formed, the solvent was removed by slow evaporation until viscous gel was formed. When the gel was completely dried, TRIS initiated a spontaneous self-combustion process acting as a fuel. The obtained ashed powders were heated at 800 °C for 5 h using a heating rate of 1 °C/min. Finally, the powders were additionally annealed at 1000 °C for 10 h using a heating rate of 3 °C/min. In the synthesis of Cr^{3+} -doped garnets an appropriate amount of chromium nitrate was added to the initial solution of metals.

For the ICP-OES analysis 16 different $Y_3Ga_5O_{12}:Cr$ and $Gd_3Sc_2Ga_3O_{12}:Cr$ garnet samples were dissolved in the diluted nitric acid (1:1, v/v) at 100 °C. The resulting solutions were diluted to an appropriate volume with deionized water. All of the solutions were prepared with ultrapure water.

An inductively coupled plasma optical emission spectrometer Perkin Elmer Optima 7000 dv was used to determine the amount of metals. X-ray diffraction (XRD) data were collected in the range of $20 \leq 2\theta \leq 70$ using Ni-filtered Cu K α radiation on a Rigaku MiniFlex II diffractometer working in Bragg-Brentano ($\theta/2\theta$) geometry. The step width and integration time was 0.02 and 1 s, respectively. The morphology of the final powders was characterized by scanning electron microscopy performed with Hitachi Tabletop Microscope TM3000 scanning electronic microscopes (SEM). Energy dispersive X-ray (EDX) analysis was performed with a Hitachi Tabletop Microscope TM3000 and Hitachi SU-70 scanning electronic microscopes.

RESULTS AND DISCUSSION

The phase purity of the synthesized garnets was determined by X-ray diffraction (XRD) analysis. The XRD patterns of the chromium-doped YGG and GSGG samples are presented in Figs. 1 and 2, respectively. As seen, the X-ray diffraction patterns of the YGG and GSGG samples doped with a different amount of chromium are very similar and confirm that in all cases the single-phase cubic garnets have been fabricated during sol-gel processing.

Scanning electron microscopy was used to investigate the surface morphology of the samples. The microstructure of the chromium-doped YGG and GSGG samples was

very similar. The representative SEM images of the samples obtained after the self-burn reaction and after heating at 1000 °C are shown in Fig. 3. The garnet samples obtained after the self-burn reaction and after heating at 1000 °C were composed of hard agglomerated plate-like crystals 1–3 μm in size.

The amount of metals in the end products was determined by inductively coupled plasma optical emission spectrometry (ICP-OES). The measurements were performed at different wavelengths. Finally, the optimum wavelengths were selected and the molar ratio of metals was calculated using the experimental data. All of the data obtained for the GSGG and YGG specimens are summarized

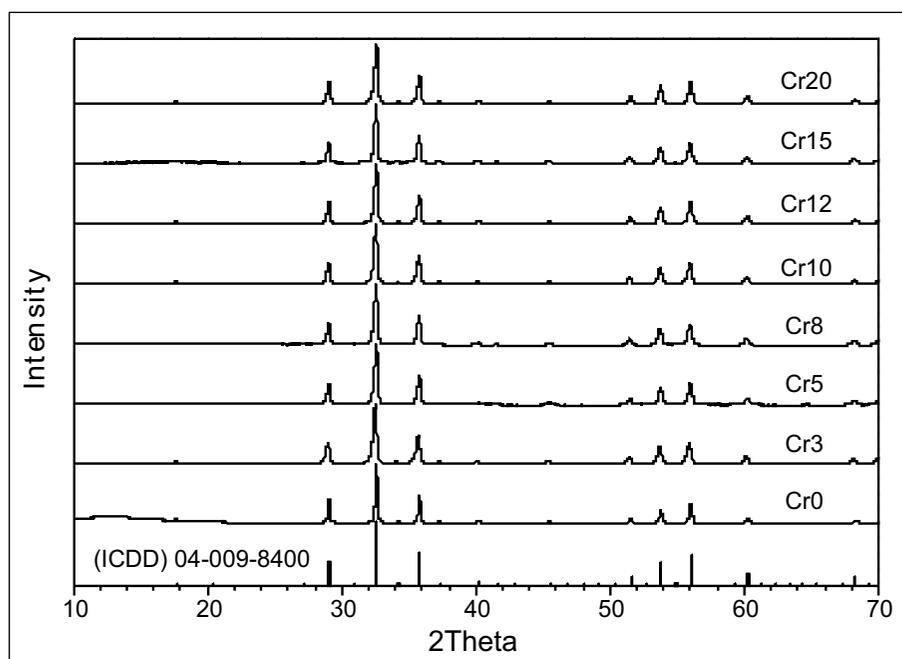


Fig. 1. XRD patterns of the YGG:Cr0-20 samples synthesized at 1000 °C. Vertical lines correspond to the standard YGG data (ICDD 04-009-8400)

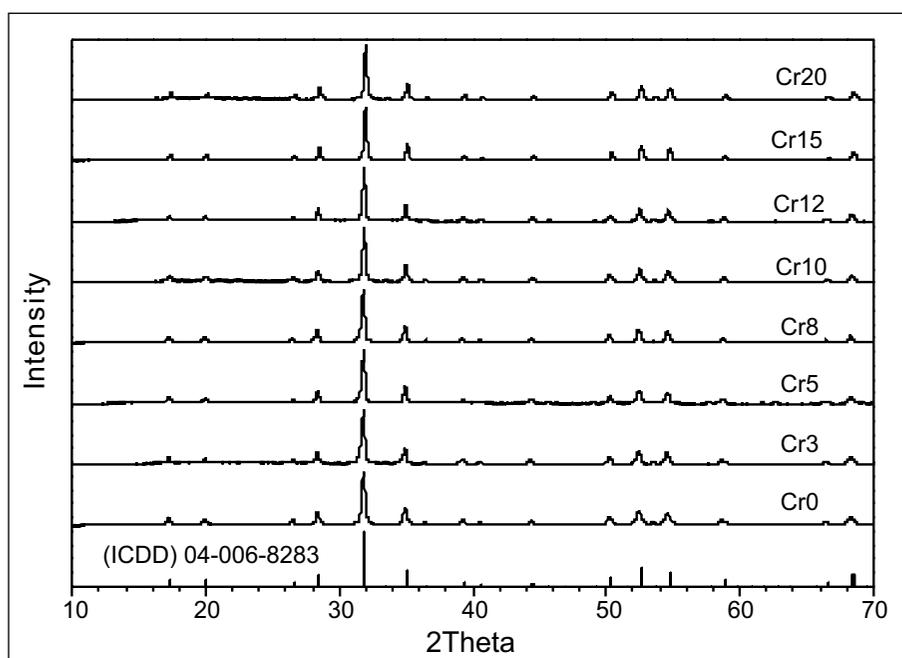


Fig. 2. XRD pattern of the GSGG:Cr0-20 samples synthesized at 1000 °C. Vertical lines correspond to the standard GSGG data (ICDD 04-006-8283)

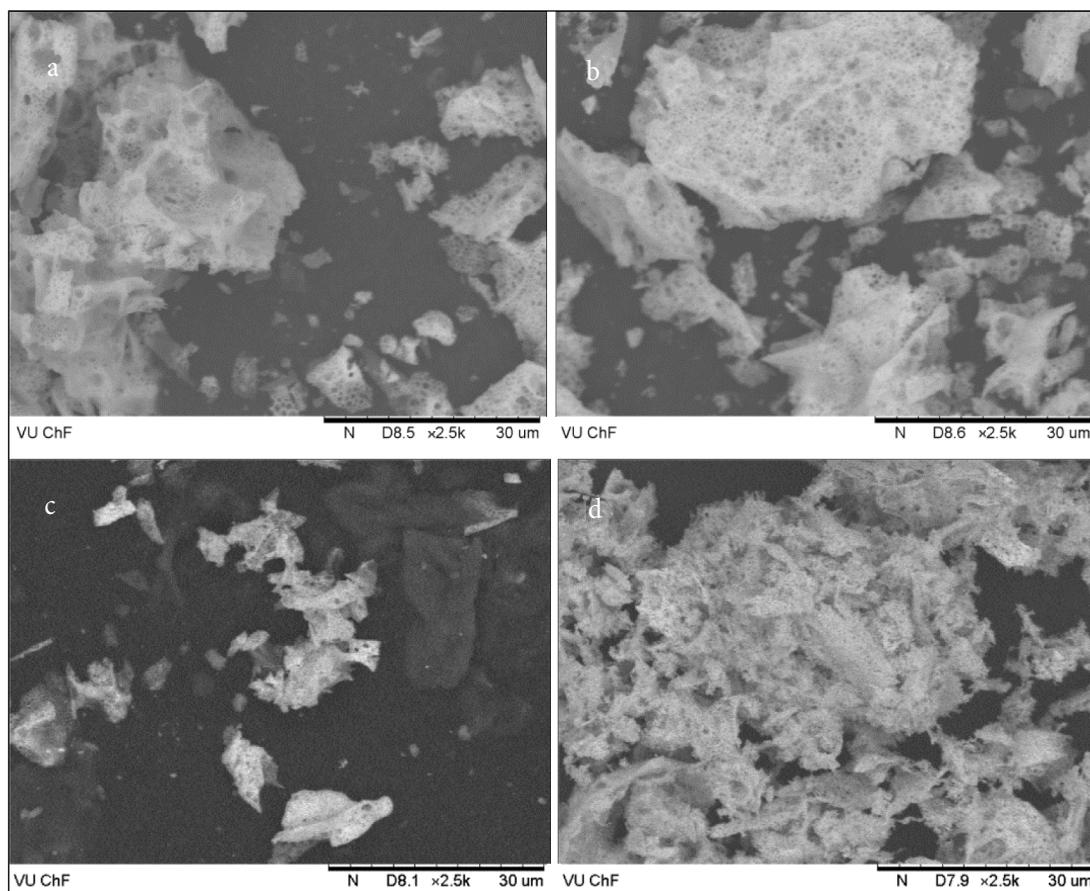


Fig. 3. SEM micrographs of YGG:Cr10 (a, b) and GSGG:Cr10 (c, d) garnet samples: ashen powders after self-burn reaction (a, c) and after heating at 1000 °C (b, d)

in Tables 1 and 2, respectively. According to the results, the determined experimental molar ratio of metals in the synthesized garnets was found to be Gd:Sc:Ga = 3:2:3 for GSGG, and Y:Ga = 3:5 for YGG. These results are in a good agreement with the nominal composition of starting metal salts. Moreover, the determined amount of chromium was the same as the desired concentration of the dopant element. Thus, the theoretical formula of GSGG and YGG is the same as the empirical formula of these synthesized garnets.

Table 1. The composition of the sol–gel derived GSGG:Cr³⁺ garnets determined by ICP-OES (n = 3)

Sample	Gd	Sc	Ga	Cr, at.%
GSGG Cr0	3.06	2.00	2.91	–
GSGG Cr3	3.08	2.00	2.94	3.4
GSGG Cr5	3.02	2.00	2.90	5.1
GSGG Cr8	3.05	2.00	2.90	8.0
GSGG Cr10	2.93	2.00	2.87	9.9
GSGG Cr12	2.96	2.00	2.91	12.5
GSGG Cr15	3.00	2.00	2.99	15.1
GSGG Cr20	2.98	2.00	2.98	19.8

Table 2. The composition of the sol–gel derived YGG:Cr³⁺ garnets determined by ICP-OES (n = 3)

Sample	Y	Ga	Cr, at.%
YGG Cr0	3	4.79	–
YGG Cr3	3	4.80	2.9
YGG Cr5	3	4.83	5.0
YGG Cr8	3	4.88	8.3
YGG Cr10	3	4.82	9.8
YGG Cr12	3	4.83	12.4
YGG Cr15	3	4.86	15.3
YGG Cr20	3	4.83	20.2

The enhancement of the performance of advanced optical materials requires the fine tuning of their composition, which has to be determined with a high accuracy. Therefore, we have additionally evaluated the chemical composition of the chromium-doped YGG and GSGG samples by energy dispersive X-ray spectroscopy in two scanning electron microscopes (Hitachi Tabletop Microscope TM3000 and Hitachi SU-70 SEM) and compared with the ICP-OES results. The results of the EDX analysis obtained for the GSGG specimens are summarized in Tables 3 and 4. As seen, the both scanning electron microscopes give comparable

EDX results with a high accuracy. Very similar results were also obtained during the analysis of the chromium-doped YGG samples (see Tables 5 and 6). Thus, we showed relevance of the EDX method for the determination of the chemical composition of the solid-state inert matrix and the dopant element. Finally, we can conclude that sol-gel processing allowed us to perform a successful synthesis of GSGG and YGG with an exact amount of chromium doped into the garnets structure.

Table 3. EDX analysis with the SEM TM300 results of sol-gel derived GSGG:Cr³⁺ garnets (n = 3)

Sample	Gd	Sc	Ga	Cr, at.%
GSGG Cr0	3.04	2.00	2.94	–
GSGG Cr3	3.15	2.00	3.03	3.3
GSGG Cr5	3.05	2.00	3.00	5.0
GSGG Cr8	3.18	2.00	2.99	8.4
GSGG Cr10	3.02	2.00	2.89	10.1
GSGG Cr12	2.97	2.00	2.98	12.3
GSGG Cr15	2.97	2.00	3.06	15.5
GSGG Cr20	2.95	2.00	2.97	19.9

Table 4. EDX analysis with the High Resolution SEM of sol-gel derived GSGG:Cr³⁺ garnets (n = 3)

Sample	Gd	Sc	Ga	Cr, at.%
GSGG Cr0	3.03	2.00	3.20	–
GSGG Cr3	2.98	2.00	3.14	3.0
GSGG Cr5	2.96	2.00	3.16	4.9
GSGG Cr8	3.07	2.00	3.02	8.0
GSGG Cr10	3.00	2.00	3.01	10.3
GSGG Cr12	2.95	2.00	2.97	11.8
GSGG Cr15	3.02	2.00	2.94	15.2
GSGG Cr20	2.93	2.00	2.99	20.0

Table 5. EDX analysis with the SEM TM300 results of sol-gel derived YGG:Cr³⁺ garnets (n = 3)

Sample	Y	Ga	Cr, at.%
YGG Cr0	3.00	4.95	–
YGG Cr3	3.00	5.05	3.1
YGG Cr5	3.00	4.87	5.4
YGG Cr8	3.00	4.94	8.08
YGG Cr10	3.00	4.96	10.3
YGG Cr12	3.00	5.03	11.7
YGG Cr15	3.00	5.11	14.6
YGG Cr20	3.00	4.99	19.8

Table 6. EDX analysis with the High Resolution SEM results of sol-gel derived YGG:Cr³⁺ garnets (n = 3)

Sample	Y	Ga	Cr, at.%
YGG Cr0	3.00	4.84	–
YGG Cr3	3.00	5.18	3.0
YGG Cr5	3.00	5.14	4.8
YGG Cr8	3.00	5.09	7.26
YGG Cr10	3.00	4.93	10.1
YGG Cr12	3.00	5.07	12.1
YGG Cr15	3.00	4.87	15.4
YGG Cr20	3.00	5.19	19.6

CONCLUSIONS

A series of the chromium-doped GSGG and YGG with a different Cr³⁺-ion concentration (3, 5, 8, 10, 12, 15 and 20 at.%) have been synthesized by an aqueous sol-gel combustion synthesis method. The X-ray diffraction patterns of YGG and GSGG samples doped with a different amount of chromium confirmed a monophasic character of the synthesized compounds. The garnet samples obtained after the self-burn reaction and after heating at 1000 °C were composed of hard agglomerated plate-like crystals 1–3 μm in size. The real chemical composition of different Cr-doped garnet structure compounds was determined by ICP-OES and EDX methods. These results were in a good agreement with the nominal composition of starting metal salts. The ICP-OES and two scanning electron microscopes gave comparable analysis results with a high accuracy. Thus, the theoretical formula of GSGG and YGG was the same as the empirical formula of these synthesized garnets. Moreover, the determined amount of chromium was also the same as the desired concentration of a dopant element.

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METALŲ PASISKIRSTYMO Cr^{3+} LEGIRUOTUOSE $\text{Y}_3\text{Ga}_5\text{O}_{12}$ IR $\text{Gd}_3\text{Sc}_2\text{Ga}_3\text{O}_{12}$ GRANATUOSE TYRIMAS ICP-OES IR EDX METODAIS

S a n t r a u k a

Šiame darbe serijos Cr^{3+} legiruoti $\text{Y}_3\text{Ga}_5\text{O}_{12}$ (YGG) ir $\text{Gd}_3\text{Sc}_2\text{Ga}_3\text{O}_{12}$ (GSGG) granatai, turintys skirtingą chromo kiekį (3, 5, 8, 10, 12, 15 ir at. %), buvo susintetinti zolių-gelių metodu ir apibūdinti. Susintetintų junginių fazinis grynumas tirtas rentgeno spindulių difrakcinės analizės (XRD) metodu, o morfologiniai ypatumai – skenuojamąja elektronine mikroskopija (SEM). Ištirta skirtingais chromo kiekiais legiruotų $\text{Y}_3\text{Ga}_5\text{O}_{12}$ (YGG) ir $\text{Gd}_3\text{Sc}_2\text{Ga}_3\text{O}_{12}$ (GSGG) granatų cheminė sudėtis. Pirmą kartą palyginti analizės rezultatai, gauti indukuotos plazmos optinės emisijos spektrometrijos (ICP-OES) ir energijos dispersijos rentgeno spindulių spektroskopijos (EDX) metodais. Nustatyta, kad susintetintų junginių cheminė sudėtis yra artima nominaliam elementų kiekiui. ICP-OES ir EDX metodais gauti rezultatai pagrindžia šių analizės metodų patikimumą.