

Cerium doped yttrium aluminium garnet modified by silicon and nitrogen

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Abstract

Compound according to the general composition $Y_3Al_{5-x}Si_xO_{12-x}N_x$, which are formally derived from the yttrium aluminium garnet $Y_3Al_5O_{12}$ (YAG) due to the substitution of oxygen by nitrogen, are of high interest for material research and application. The required charge compensation due to the replacement of oxygen by nitrogen is achieved by the appropriate substitution of aluminum by silicon.

This paper deals with the solid state synthesis and optical properties of $Y_3Al_{5-x}Si_xO_{12-x}N_x$ samples doped by trivalent cerium and more specifically with the effect of the O/N and Al/Si ratio on the optical properties. It turned out that the incorporation of Si and N yields a red shift of the 5d-4f emission band of Ce^{3+} , whereby the extent of the red shift can be correlated to the composition of the host lattice.

Keywords: YAG, optical properties, luminescence

GRANAT ITROWO-GLINOWY DOMIESZKOWANY CEREM I MODYFIKOWANY KRZEMEM ORAZ AZOTEM

Interesującym materiałem na luminofory jest związek $Y_3Al_{5-x}Si_xO_{12-x}N_x$, który stanowi pochodną granatu YAG z podstawieniem azotu w miejsce tlenu. Dla niezbędnego skompensowania ładunku spowodowanego tym podstawieniem zastąpiono krzemem część atomów glinu.

W artykule opisany został sposób syntezy związków $Y_3Al_{5-x}Si_xO_{12-x}N_x$ z trójwartościowym cerem jako aktywator oraz wpływ podstawień O/N i Al/Si na własności optyczne. W wyniku takiego podstawienia występuje przesunięcie emisji promieniowania w stronę większej wartości długości fali.

Słowa kluczowe: YAG, właściwości optyczne, luminescencja

Introduction

Yttrium aluminium garnet (YAG, $Y_3Al_5O_{12}$) is an important ceramic material. By doping with rare earth ions it has found a wide range of applications: LASERs, scintillators, phosphors (FLs and LED) [1]. Cerium doped YAG (YAG:Ce) is a phosphor or scintillator with wide range of applications. The emission spectrum is characterized by 5d-4f Ce^{3+} transition [2]. This garnet emits yellow light when excited by blue, ultraviolet or x-ray electromagnetic radiation. It is used in white light-emitting diodes, as a coating layer onto the blue InGaN diode, converting part of the blue light into yellow to obtain white light [3]. Nowadays, cerium is a commonly applied dopant in YAG phosphors for white LED. The white light can have different temperature color: cold and warm [4]. Almost all materials containing nitrogen have orange color, that give us possibility to change color of YAG by doping it with nitrogen. Within the Y-Al-Si-O-N system several compositions, e.g. α - and β -SiAlONs, Y_2SiAlO_5N and $YSi_2AlO_4N_2$ are of technical importance. These compounds are applied as high performance structural ceramics [5] and as host lattices for luminescent materials [6, 7]. In the same way the trials of changing the properties of YAG:Ce have been carried out.

One of the low cost way to prepare these materials is a carbothermal reduction and nitridation (CRN) of silicate

or aluminosilicate. The CRN technique has been proven as very successful specially for preparation of SiAlONes [8]. The carbo-reduction/nitridation process involves a composite sequence of reactions which depend on the nature of the reactants and the parameters used in the process. It is generally accepted that gas phase transport plays an important role in the reactions within the powder. Transport of N_2 to the reaction site and CO away from the reaction site is of crucial importance. The reactions of C or CO with silica or silicates produces a significant partial pressure of gaseous SiO within the powder at $>1400^\circ C$ [9].

Experimental part

The samples with the general formula $(Y_{1-a}Ce_a)_3(Al_{1-x}Si_x)_5O_{12-5x}N_{5x}$ ($a = 0,2$; $x = 0 - 1$) were prepared by a conventional solid-state reaction. Carbon was used on the amount from 0,5 to 1,5% total weight of samples, hypermer KD1 was used on the amount of 0,03% total weight of samples.

The stoichiometric amounts of raw powders Y_2O_3 (99.99%, Treibacher), Al_2O_3 (99.99%, Alfa Aesar), Si_3N_4 (<98%, UBE), CeO_2 (99.99%, AtomicChemicals) as an activator and AlF_3 (<99.9%, Aldrich) as a flux were grinded with isopropanol in an agate mortar, dried for 2 hours at $120^\circ C$ and annealed

for 8 hours in an N_2 or N_2/H_2 atmosphere at temperatures varied from 1550 to 1650 °C in a tube furnace.

An APD 1700 Philips diffractometer and a Rigaku MiniFlex II diffractometer were used for taking the powder diffraction patterns. The XRD patterns were collected in the 2θ range of 10–60° with a step size of 0,02° and a scanning speed of 5° per minute using $Cu K\alpha_1$ radiation with $\lambda = 1.542 \text{ \AA}$ (for APD 1700 Philips diffractometer) and $\lambda = 1.5406 \text{ \AA}$ with nickel filter (for Rigaku MiniFlex II diffractometer). Excitation and emission spectra were measured with an Edinburgh Instruments FS900 spectrometer equipped with 450 W Xe arc lamp, mirror optics for powder samples and cooled single photon counting photomultiplier (Hamamatsu R2658). Excitation and emission spectra were recorded in the regions of 250 – 550 nm and 460 – 800 nm respectively. Philips powder U728 was used as a standard. Reflection spectra were recorded on ARC SpectraPro-300i (Acton Research Corporation) spectrometer equipped with 450 W Xe arc lamp, single photon counting photomultiplier and integration sphere. Reflection spectra were recorded in the region of 250 – 800 nm with the steps of 1 nm. Barium sulfate ($BaSO_4$, 99,998% purity, Alfa Aesar, Germany) was used as white standard. All measurements were carried out at room temperature.

Results and Discussion

YAG with Carbon inside sample

The best solution for the creation of reductive conditions is homogeneous distribution of carbon inside the sample. At high temperatures carbon should react with oxide contained in the sample creating carbon monoxide (gas), protective atmosphere should make impossible to oxidize Si_3N_4 and this to things enables incorporation of nitrogen in a host lattice. Doped nitrogen should come from solid phase (silicon nitride) and from the gas atmosphere.

Usually the powder YAG:Ce has the yellow color. The color of the powder has been changed on orange as a result of building nitrogen. That allows to the preliminary recognition of the good reduction process.

Figure 1 represents the typical result of tests. Very hard, sinter and yellow color samples were obtained. After cutting longitudinal three phases could be observed, yellow without nitrogen, orange with nitrogen and grey with carbon. Rise of the flow of the nitrogen gas from 5 to 10 l/h causes decrease of the amount of yellow phase, however the amount of a grey phase increases (figure 2).

The atmosphere have not guaranteed reductive conditions during synthesis. Too big partial pressure of oxygen in the furnace's atmosphere have oxidized the nitrogen from the sample. Small quantity of the phase with nitrogen have been found between the phase with oxidized nitrogen and the phase with not reduced carbon (figure 1). Increase of the flow of nitrogen in the furnace have caused a decrease of the amount of the reduced carbon contained in the sample. Despite that fact, phase without nitrogen was also obtained. Results show that nitrogen does not carry out its role as a protective gas, even when its flow has been increased.

It was expected that the change of gas atmosphere (nitrogen = 95%, hydrogen = 5%) in a furnace could eliminate phases without nitrogen from the garnet through decrease of a partial pressure of oxygen. Unfortunately the carbon has been found inside all samples and there was no possibility to separate both phases. Figure 3 shows typical samples as obtained.

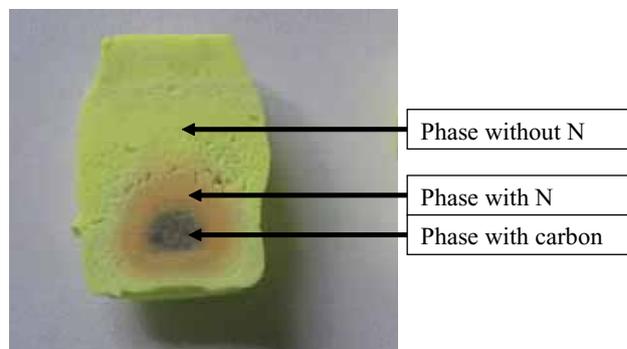


Fig. 1. Typical results of YAG sample with carbon (N_2 atm. 5 l/h)

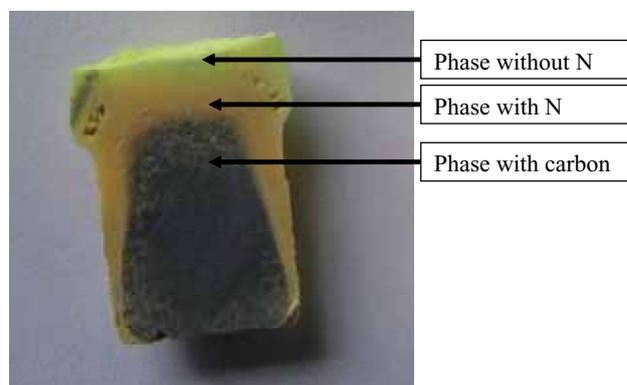


Fig. 2. Typical results of YAG sample with carbon (N_2 atm. 10 l/h)

YAG with Carbon outside samples

Three different ideas about carbon outside samples were checked. In the first method the second big corundum crucible with active carbon has been used. Inside the first crucible a smaller one with a sample was inserted. In the second idea two graphite pads below and above crucible with a samples have been used. In the third idea a graphite chamber with two graphite stoppers with holes have been used. The last idea has guaranteed the best reduction atmosphere for the reaction. However the manufacture of chambers has been quite difficult, and their lifetime very short. In this chapter only the results with graphite chamber are presented. Figure 4 shows how a gas flows inside the graphite chamber.

On this stage of investigation dispersant KD1 was used as a dispersant of Si_3N_4 [10]. The results show that samples with hypermer KD1 have been more fragile, less sintered and easier to mill after annealing.

Figure 5 shows X-ray diffraction patterns of YAG doped different concentration of silicon and nitrogen. The pure crystalline phase was obtained for the sample with concentration of nitrogen equal 0,25. For the next two samples XRD patterns show that the samples contained unknown phase.



Fig. 3. Typical results of YAG sample with carbon (N₂/H₂ atm. 10 l/h)

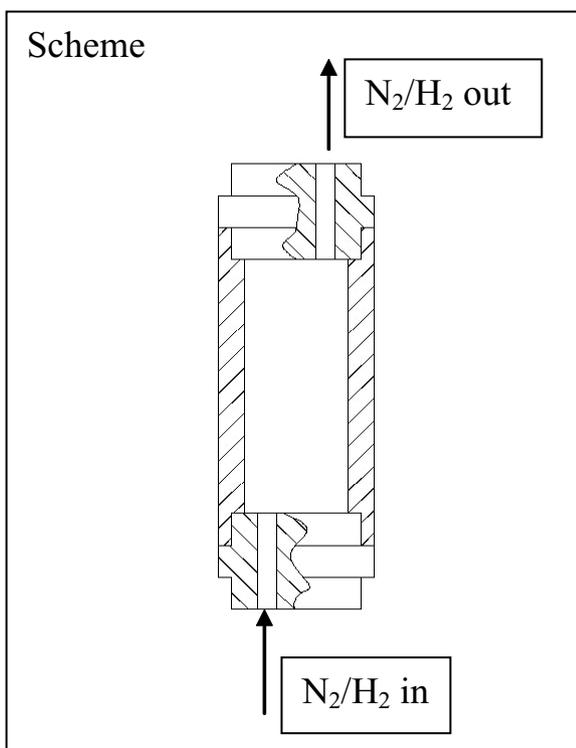


Fig. 4. Schematic of a fixed graphite chamber

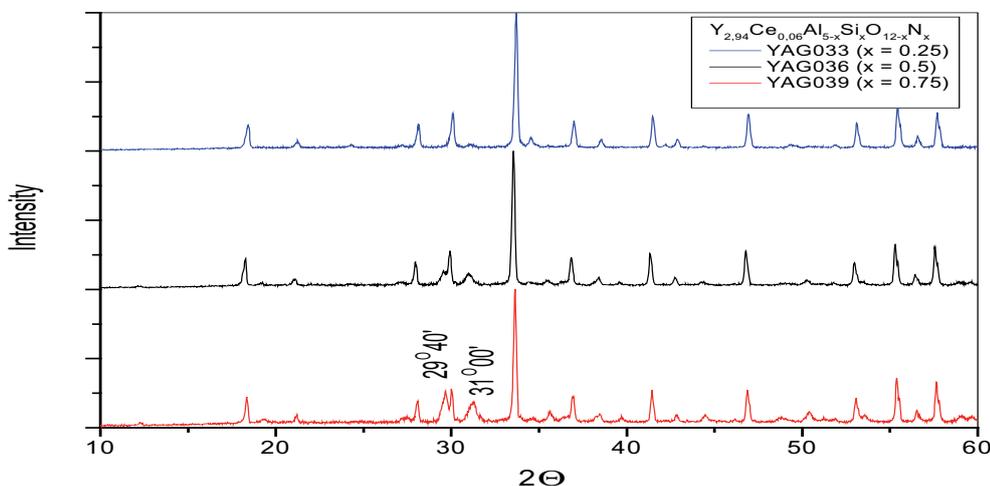


Fig. 5. Powder XRD patterns of as synthesized samples Y_{2,94}Ce_{0,06}Al_{5-x}Si_xO_{12-x}N_x with different concentration of nitrogen (x = 0.25; 0.5; 0.75)

Reflection spectra (Figure 6) shows strong absorption band at 450 nm - Cerium excitation point. The samples Y_{2,94}Ce_{0,06}Al_{4,75}Si_{0,25}O_{11,75}N_{0,25} reflects about 87%, the samples with higher concentration of Si₃N₄ reflects about 10% less. Different sharp curves in the range 350 - 420 nm for both samples were observed.

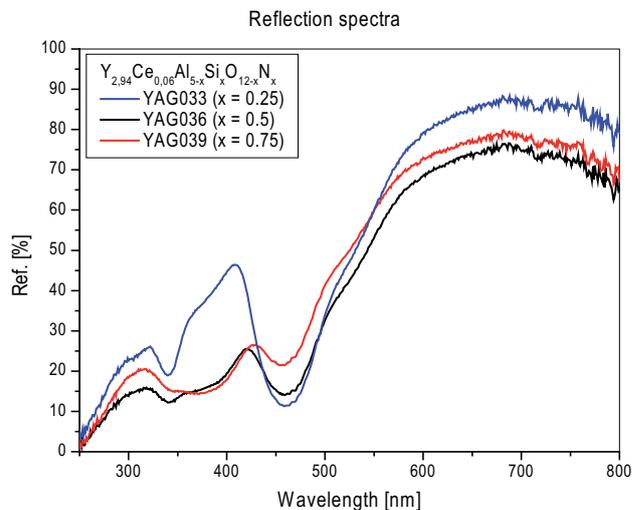


Fig. 6. Influence of concentration of nitrogen for a reflection of the samples Y_{2,94}Ce_{0,06}Al_{5-x}Si_xO_{12-x}N_x (x = 0.25; 0.5; 0.75)

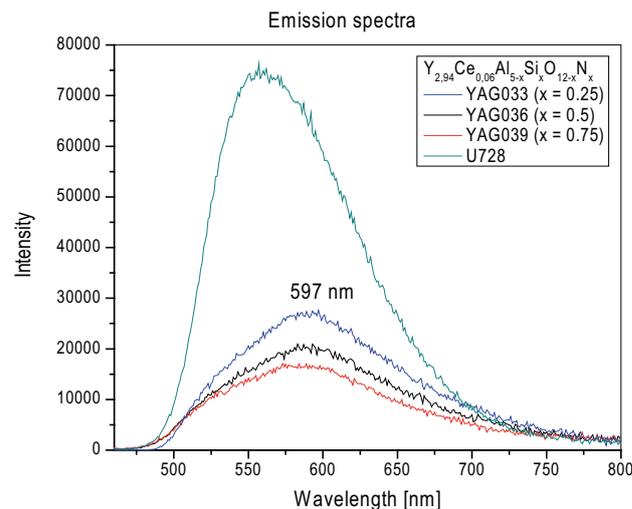


Fig. 7. Influence of concentration of Si and N for emission spectra of the samples Y_{2,94}Ce_{0,06}Al_{5-x}Si_xO_{12-x}N_x (x = 0.25; 0.5; 0.75), U728 – standard YAG

The emission spectra of Y_{2,94}Ce_{0,06}Al_{5-x}Si_xO_{12-x}N_x (x = 0.25; 0.5; 0.75) are shown in Figure 7. The obtained samples were compared with the reference YAG (Philips U728). All samples have been excitation at 450 nm. Smaller intensity of emission peaks and shift to the right in comparison with reference sample were observed.

Conclusion

The atmosphere N_2 / H_2 assures better conditions of annealing than the nitrogen atmosphere. There was no possibility of burning the carbon totally out of the sample in both atmosphere. The crucibles with the active carbon, as well as graphite pads have not guaranteed right reductive atmosphere inside a furnace. In both cases samples contained two phases: one with nitrogen and one without. There was no possibility of separating them. To obtain good samples a hermetic furnace and the atmosphere without oxygen or reduction source outside sample are required.

Variation of O/N ratio in $Y_{2,94}Ce_{0,06}Al_{5-x}Si_xO_{12-x}N_x$ ($x = 0 - 1$) composition have influenced on luminescent properties of the material. A composition according to the this formula with $x = 0.25; 0.5; 0.75$ shows an emission spectrum with a broad Ce^{3+} emission band centered at 597 nm. The highest luminescence intensity have been observed for the $Y_{2,94}Ce_{0,06}Al_{4,75}Si_{0,25}O_{11,75}N_{0,25}$. The influence of the temperature and excess of silicon nitride will be reported in the future.

References

- [1] Mares J.A., Nikl M., Beitlerowa A., Solovieva N., D' Ambrosio C., Blazek K., Maly P., Nejezchleb K., Fabeni P., Pazzi G.P.: Nuclear Instruments and Methods in Physics Research A, 537 (2005) 271-275.
- [2] Dong Y., Zhou G., Xu J., Zhao G., Su F., Su F., Su L., Zhang G., Zhang D., Li H., Si J.: Materials Research Bulletin, 41 (2006) 1959-1963.
- [3] Yang Z., Li X., Yang Y., Li X.: Journal of Luminescence, 122-123 (2007) 707-709.
- [4] Edited by Ronda C.; Juestel T. chapter; Luminescence form theory to applications; Wiley-vch 2008.
- [5] Sopicka-Lizer M., Piekarczyk J.: Key Engineering Materials, 206-213 (2001) 429-432.
- [6] Xie R.-J., Hirotsaki N., Mimoto M., Yamamoto Y., Suehiro T.: J. Phys. Chem. B, 108 (2004) 12027-12031
Barrg R.: Glass, 68 (1991) 32-35.
- [7] Krevel W.H.: J. Solid State Chem., 165 (2002) 19-24.
- [8] Dong Y., Zhou G., Xu J., Zhao G., Su F., Su L., Li H., Si J., Qian X., Li X., Shen J.: Journal of Crystal Growth, 286 (2006) 476-480.
- [9] Li J.G., Ikegami T., Lee J.H., Mori T.: J. Am. Ceram. Soc., 83 [4] 961-63 (2000).
- [10] Sopicka-Lizer M.: SIALON ceramics from carbothermally derived powder - physical chemistry of manufacturing and properties; WPS, 2000.

