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Investigation of Colour Centres in Gadolinium Gallium Garnet Crystals

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Absorption spectra of ultraviolet-irradiated single crystals of gadolinium gallium garnet are investigated. Colour centre bands are observed at 440 and 320 nm. The absorption can be enhanced by doping with Tb, and suppressed by doping with Eu. Annealing treatments under a low partial oxygen pressure cause a decrease of the absorption after irradiation. A similar effect is found after heating the garnet covered with a silicon layer. An increased colorability is obtained after annealing in oxygen. Glow curves and thermally stimulated electrical conductivity show the recombination of charge carriers at rare earth sites. From these observations it is concluded that the colour centre bands are due to trapped electrons, possibly at interstitial gallium sites.

Die Absorptionsspektren von UV-bestrahltem einkristallinem Gadolinium-Gallium-Granat werden untersucht. Bei 440 und 320 nm werden Farbzentrenbanden beobachtet. Die Absorption kann durch Dotierung mit Tb verstärkt und durch Dotierung mit Eu abgeschwächt werden. Durch Tempern bei niedrigem Sauerstoffdruck wird eine Abschwächung der Absorption nach der Bestrahlung gefunden. Ein ähnliches Verhalten zeigt sich auch, wenn eine mit Si bedampfte Granatprobe getempert wird. Beim Tempern in Sauerstoff bemerkt man eine Zunahme der Absorption nach Bestrahlung. Glow-Kurven und eine thermisch stimulierte elektrische Leitfähigkeit weisen auf Rekombinationen von Ladungsträgern mit den Dotierungen hin. Aus den Beobachtungen wird geschlossen, daß die Farbzentrenbanden durch Elektronen, welche möglicherweise durch interstitielles Gallium eingefangen sind, verursacht werden.

1. Introduction

Colour centres in the transparent garnets $\text{Y}_3\text{Ga}_5\text{O}_{12}$ (YGG) and $\text{Y}_3\text{Al}_5\text{O}_{12}$ (YAG) have been studied by several authors [1 to 4]. Ultraviolet or γ -irradiation at room temperature leads to the formation of a number of broad, structureless absorption bands in the wavelength region 300 to 700 nm. The formation of colour centres is generally unwanted since they limit the applicability of these crystals as a host for solid state lasers. A visible coloration is also undesirable in crystals used as artificial jewels. Of these materials γ -irradiated YAG has been investigated in most detail. The addition of rare-earth ions to YAG influences both the strength of the absorption bands and the position of the maximum. The absorption bands disappear when the irradiated crystals are heated; in some cases the thermal bleaching is accompanied by thermoluminescence with an emission spectrum which is characteristic of the trivalent rare-earth activator. The absorption bands have not been identified with certainty, but are probably due to electrons trapped at anion vacancies and holes trapped at oxygen ions [2].

In an earlier publication [5] we have discussed the use of rare-earth-activated luminescence for the study of crystal defects in the related garnet $\text{Gd}_3\text{Ga}_5\text{O}_{12}$

(GGG). The perfection of this material is highly important for the application as a substrate for magnetic thin films which are used in bubble devices and magneto-optic devices. Since GGG also satisfies the demands of a jewels, viz. transparency in the visible spectrum, a high refractive index, chemical inertness, and sufficient hardness, and since it can be easily doped, it is of interest to investigate the possibility of colour centre formation. It was observed that ultraviolet irradiation often produced a brownish colour in GGG crystals. We shall present here data of the absorption and luminescence spectra of undoped GGG and of GGG doped with Tb and Eu. Special attention will be paid to a possible suppression of the visible coloration.

2. Experimental

The crystals were grown by the Czochralski method [6]. Because of the high melting point an iridium crucible was used which was insulated by zirconia granules [7], and heated in an rf coil. A neutral atmosphere is required to protect the crucible from oxidation. An oxidizing atmosphere diminishes the evaporation of Ga_2O_3 . Nitrogen with 2% of oxygen was used as a compromise. The purity of the starting materials was 99.99%. We obtained the Gd_2O_3 from Michigan Chemical Corporation and the Ga_2O_3 from Alusuisse. Each of these oxides was pressed to tablets to enable the fusion in one run. The molar ratio in the melt of the undoped garnet was $\text{Gd}_2\text{O}_3:\text{Ga}_2\text{O}_3 = 3.02:4.98$. The crystal diameter was controlled by the weight method [8]. The weight of the insulation material, the crucible, and the melt was compared with a linearly decreasing reference weight. The difference was minimized by means of power corrections.

Crystal 1 was nominally pure $\text{Gd}_{3.02}\text{Ga}_{4.98}\text{O}_{12}$. A spectrochemical analysis of the impurity content of an undoped crystal is given in Table 1. For crystals 2

Table 1

Spectrochemical analysis of the impurity content of an undoped $\text{Gd}_3\text{Ga}_5\text{O}_{12}$ crystal

element	Mg	Si	Cr	Fe	Ni	In	Y	Eu	Yb
concentration weight (ppm)	10	30	3	30	20	5	50	20	40

and 3 the melt contained 0.1 wt% of Tb and Eu, respectively, and 2.5 wt% of Eu was added to the melt for crystal 4.

On the base of the scanty data in the literature [9] we estimate the segregation coefficient of Tb and Eu to be 1.0 and 0.8, respectively.

The resulting number of rare-earth atoms per formula unit is therefore in crystal 2: 0.003 Tb, in crystal 3: 0.0025 Eu, and in crystal 4: 0.075 Eu.

The garnet specimens used for our investigations were (111) platelets of about 1 mm thickness, cut and polished from [111] boules.

The crystals were irradiated at room temperature with the light of an HP 125 mercury lamp, filtered through 3.5 cm water and a Schott BG 21 glass filter. The wavelength range transmitted through this filter combination is 300 to 1000 nm. The crystals were irradiated until a saturation value of the optical absorption at 450 nm was reached, which took about 4 h for platelets of 1 mm thickness. Immediately after irradiation the absorption spectrum was recorded with a Cary-14 spectrometer.

Fig. 1. Room temperature absorbance A of a Tb-doped GGG platelet; thickness 1 mm. Lower line: untreated sample. Upper line: after 4 h irradiation with a mercury lamp

For the measurement of glow curves, the samples were irradiated at 77 K (or in some cases at room temperature), after which the temperature was increased by 10 K/min to approximately 600 K. Glow curves were measured for the strong Tb^{3+} emission line at 385 nm or the Eu^{3+} emission line at 708 nm.

3. Results

3.1 Absorption measurements

Fig. 1 shows the absorption spectrum of a Tb-doped single crystalline GGG platelet before and after UV irradiation. Before the first measurement the samples were annealed at 500 °C in air to remove polishing stresses and residual absorption. The sharp bands near 310 nm are due to crystal field transitions of Gd^{3+} . The spectra were taken with dry air in the reference beam, and accordingly the absorbance¹⁾ of 0.1 above 400 nm in the unirradiated sample is due to reflection losses. The radiation-induced absorption is more clearly observable in Fig. 2, where the difference of the absorbance before and after irradiation is plotted for three different crystals. Two broad bands are observed with maxima near 440 nm (2.82 eV) and 320 nm (3.87 eV). The high-frequency side of the ultraviolet absorption band is relatively inaccurate since it is superposed on the strong internal Gd transition. Further, the original spectrum of sample 4, with the highest Eu concentration, also shows sharp peaks due to crystal field transitions of the Eu^{3+} ions. It is evident from Fig. 2 that the presence of Tb ions strongly enhances the intensity of the absorption, while Eu suppresses the band in the visible region. The influence of an annealing treatment on the colorability of the crystals is shown in Fig. 3. The samples were first kept in a stream of oxygen at 1500 °C for 24 h and irradiated after quenching in air. Comparison with Fig. 2, which was measured on samples annealed in air at 500 °C, shows that the absorbance is increased considerably. When the crystals are irradiated after a 1500 °C anneal in flowing nitrogen (partial oxygen pressure $\approx 10^{-6}$ atm), the intensity of the colour centre bands is much lower. Repeated annealing treatments show that the effect is reversible. It is known

¹⁾ The absorbance is defined as $\lg(I_{\text{ref}}/I_{\text{sample}})$.

Fig. 2. Increase of absorbance after UV irradiation of 1 mm thick GGG samples. — Tb-doped sample 2; - - - undoped sample 1; - · - · - Eu-doped sample 4

Fig. 3. Increase of absorbance after UV irradiation of 1 mm thick GGG samples with Tb or Eu dopes. Before irradiation the samples were annealed at 1500 °C in O₂ or N₂

that at 1500 °C some Ga₂O₃ evaporates from the surface, leaving a white crust of 3 Gd₂O₃:1 Ga₂O₃ [10]. Therefore it was necessary to repolish the surfaces of the crystals slightly between the different anneal treatments. Since the absorption changes are reversible, however, we may assume that the effect is not due to an irreversible Ga loss, but instead is related to the partial oxygen pressure during the heat treatment. This assumption is further justified by the following experiment.

Both sides of a circular platelet were partly covered with a sputtered layer of silicon of about 3.5 μm thickness. After annealing at 700 °C in air the silicon was removed by means of an etchant containing HF. From similar experiments on mixed rare-earth iron-gallium garnet [11] it is known that a silicon anneal as described above is equivalent to an anneal under a low partial oxygen pressure. We now show that the GGG crystals behave analogously. After ultraviolet irradiation the extra absorbance at 440 nm of the silicon-treated part of the crystal was $\Delta A_{440} = 0.022$, while the uncovered part showed $\Delta A_{440} = 0.081$. This difference in coloration was directly visible to the eye. A similar effect was measured for the absorption band near 340 nm: Si-treated $\Delta A_{340} = 0.049$, untreated $\Delta A_{340} = 0.107$. In the absence of accurate reflection data it is difficult to calculate the absorption coefficient α for the two absorption bands accurately. Using a constant reflection coefficient $R = 0.115$ we have estimated the absorption coefficient. After Si or N₂ annealing the ratio $\alpha_{340}/\alpha_{440}$ was found to increase, showing that the peaks are due to different centres. The ratio between the two colour centre bands is also influenced by the irradiation procedure. We found that the 440 nm band could be bleached by irradiation at this wavelength. The decrease of the 440 nm band is accompanied by an increase of the 340 nm absorption.

As mentioned above thermal bleaching of the colour centre bands is also possible. A 10 min anneal at 220 °C caused a 20% decrease of the absorption constant α_{440} , while 10 min at 250 °C were sufficient to produce a 40% decrease. A very slow decrease is already observed when the samples are kept in the dark at room temperature. The decay curves could not be described by a monomolecular or bimolecular process with a single relaxation time.

3.2 Luminescence measurements

In an earlier paper [5] we have discussed the thermoluminescence occurring after X-ray excitation at low temperatures. When Tb- or Eu-doped samples are irradiated with X-rays or UV light at 77 K, an increase of temperature causes a luminescence that is characteristic of Tb^{3+} and Eu^{3+} ions, respectively. Between 77 and 350 K at least three peaks were found in the glow curves of GGG:Tb and GGG:Eu. We have now extended these measurements to higher temperatures. Between 350 and 700 K one more peak is observed at about 445 K for Tb and 490 K for Eu (Fig. 4 and 5). Therefore at least four trapping centres with different thermal activation energies are present in this garnet. A measurement of the dc conductivity of GGG:Tb after irradiation at 77 K showed that a thermally activated conductivity peak accompanies the Tb luminescence. This is a direct proof that the glow peaks are caused by the thermal release of electrons or holes from their trapping centres. An experiment to determine the sign of the charge carriers released at this temperature was not successful, however. A comparison of the position of the glow peaks with the temperature, necessary for thermal bleaching of the absorption bands, does not show a clear relationship. In other words, we are not able to establish a relationship between the traps evinced by the peaks in the glow curves and the centres responsible for the absorption bands.

4. Discussion

The experimental results can be summarized as follows:

1. The presence of Tb ions enhances the intensity of the absorption, while Eu suppresses the formation of colour centres.
2. High temperature annealing under a lowered partial oxygen pressure or in contact with a reducing element like Si, suppresses the formation of colour centres.

3. Thermoluminescence and thermally stimulated conductivity experiments show the presence of several electron and hole traps.

From thermoluminescence experiments on YAG doped with rare-earth ions, Batygov et al. [3] concluded that Tb^{3+} acts as a hole trap, while Eu^{3+} is an electron trap. From our earlier measurements on luminescence in GGG [5] we concluded that the same model is applicable for this material.

Further evidence for the occurrence of charged traps is obtained from our observation of a thermally stimulated electrical conductivity which accompanies

Fig. 4. Glow curves of a Tb-doped GGG crystal after UV irradiation at 77 K. Heating rate ≈ 10 K/min

Fig. 5. Glow curve of a Eu-doped GGG crystal after UV irradiation at 77 K. Heating rate ≈ 10 K/min

the luminescence. The opposite effect of Eu and Tb on the colour centre formation is then in accordance with the assumption that these rare-earth ions trap charge carriers with opposite signs. We therefore conclude that the colour centres are due to trapped electrons. As argued before, the reversible effect of annealing under varying partial oxygen pressures can be explained in terms of a reversible oxygen loss. By analogy with $Y_3Fe_5O_{12}$ [12] we suppose that oxygen vacancies are formed, which act as electron trapping centres. Since annealing at a low oxygen pressure inhibits the colour centre formation, electrons trapped at oxygen vacancies cannot be responsible for the absorption bands under discussion. Instead we have to conclude that the oxygen vacancies are competing traps, thereby suppressing the coloration of GGG.

Apart from oxygen vacancies and unidentified impurity centres the only possible electron trapping centres are cation interstitials. In GGG it is very well possible that some of the relatively small Ga ions are accommodated on interstitial sites, e.g. the b sites of the garnet structure. A possible candidate for the colour centre in this material is therefore an electron trapped at an interstitial Ga ion.

In conclusion, we have shown that the formation of colour centres in GGG under the influence of UV light can be suppressed by a high-temperature treatment under reducing conditions. The colorability is further diminished when the crystals are doped with Eu ions.

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