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Optical properties of color centers in calcium-stabilized gadolinium gallium garnets

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The addition of small amounts of calcium during the crystal growth of large-diameter, gadolinium gallium garnet (GGG) crystals creates color centers that absorb in the near-uv region of the spectrum. Ultraviolet and γ-ray irradiation of the crystals produced changes in the intensities of the uv color-center bands along with a broad absorption throughout the visible spectrum. The color center that gives rise to an absorption band at 350 nm serves as a photoionizable donor center so that uv excitation results in a visible coloration of the crystals. The effects of oxidation and reduction treatments on the strength of the color-center bands and on the radiation response of the material were examined. Photoluminescence bands were observed in both reduced GGG crystals as well as crystals that were irradiated with neutrons. Visible coloration is likely to occur during flashlamp pumping of laser rods that utilize large-diameter GGG crystals as the laser host. The changes in the optical properties of the material under uv excitation indicate that the addition of small amounts of calcium to assist in the growth of large-diameter crystals is likely to result in the degradation of laser performance.

I. INTRODUCTION

The optical absorption of defects in gadolinium gallium garnet crystals ($Gd_3Ga_5O_{12}$ or GGG) is of appreciable significance when considering these crystals as host materials for solid-state lasers. The defects can arise through processes inherent in the crystal growth, through postgrowth thermal treatments, or under exposure to irradiation or flashlamp excitation. Examples of these centers are impurity ions, which are present in the starting materials or which may be intentionally added during the crystal-growth process, and centers associated with cation or anion vacancies. In growing large-diameter single crystals for high-power laser applications, small amounts of dopants, such as calcium ions, are sometimes included in the melt to assist in the crystal growth. The formation of color centers, which may occur as a consequence of this doping, may alter the absorption properties of the crystal and degrade the laser performance of scaled-up, high-power solid-state lasers. Our interest in the optical properties of these defect centers is twofold. The optical absorption of these defects in the as-grown state, and the changes in their absorption due to optical pumping, are of fundamental importance in the consideration of these materials as hosts for solid-state lasers. In addition, investigation of the efficient luminescence of various color centers in oxide crystals may lead to color-center lasers analogous to those in alkali-metal-halide crystals.

II. EXPERIMENTAL METHODS AND RESULTS

A. As-grown samples

Crystals of Czochralski-grown GGG were purchased from Allied Corporation, Charlotte, North Carolina. The crystals were cut from 3-in.-diam wafers into optical samples with approximate dimensions of $10\times10\times0.5$ mm^3. During sample growth, small amounts of calcium (approximately 20–50 ppm) were added to the starting materials for the stabilization of the large-diameter boules.[1] Trace amounts of transition-metal and rare-earth impurities were also detected in the crystals. A Perkins-Elmer Lambda-9 spectrophotometer was used to measure the optical absorption of the samples. A room-temperature absorption spectrum for an as-received crystal is shown in Fig. 1. There was very little optical absorption throughout the visible region. In the near-uv region, we observed a broad absorption band which extended from 400 nm to the band edge at approximately 230 nm (~5.4 eV). In addition, there was a series of sharp lines from the $4f$ states of Gd^{3+} corresponding to the $^8S\rightarrow{}^6P$, ^6I, and ^6D transitions at 310, 275, and 245 nm, respectively.[2]

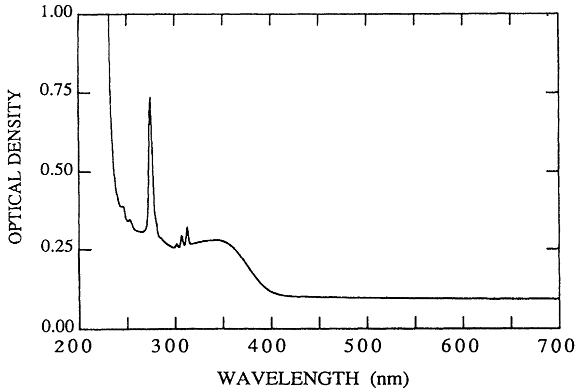

FIG. 1. Optical-absorption spectrum of a 0.5-mm-thick GGG crystal.

The broad absorption band has been previously attributed to the presence of color centers that occur as a consequence of doping the crystals with calcium.[3] Ca^{2+} ions in the crystal require the presence of a charge compensator to maintain the overall charge neutrality of the crystal. It has been proposed that oxygen vacancies associated with Ca^{2+} impurities, or O_2^{2-} centers, are responsible for the charge compensation in these materials.[3,4] Through the use of absorption and luminescence spectroscopy on crystals with various thermal and irradiation treatments, we have determined that there exist several defects which contribute to the observed near-uv absorption in these GGG crystals.

B. Effects of oxidation and reduction

Crystals of GGG were oxidized by heating the crystals for 30 min in an oxygen atmosphere, or reduced by annealing in graphite immersed in flowing N_2 gas. Both oxidation and reduction experiments were carried out at temperatures ranging from 600 to 1800 K. The absorption and emission spectra of the crystals were measured following these thermal treatments. At temperatures below 1300 K, oxidation led to an increased absorption at 350 nm and a slight decrease in the absorbance near 250 nm. Reduction of the crystal resulted in the reverse effect. A comparison of the absorption spectra following oxidation and reduction at 1173 K is shown in Fig. 2. The simplest interpretation of these results is that there existed optical defects which changed their valence state during oxidation and reduction at temperatures below 1300 K. At temperatures above 1300 K, the optical absorption of the defects no longer showed this reciprocal relationship between oxidation and reduction. Oxidation of the crystals between 1300 and 1700 K produced very little change in the optical-absorption spectra from that observed following oxidation at 1173 K. This indicated that the defects associated with the 350-nm absorption reached some saturation level, perhaps in relation to the amount of calcium impurities present in the crystal. Therefore, we believe that the oxidation of the samples resulted in valence changes in the color centers and impurities already present in the crystal. The reduction of the GGG crystals at temperatures in excess of 1300 K altered the structure of the material. At 1473 K the crystals became milky white in appearance, and at temperatures above 1673 K, small drops of metal appeared on the edges of the sample due to the extraction of metal cations from the material. X-ray diffraction of GGG crystals showed that the samples changed from crystalline to amorphous after reduction at temperatures above 1473 K.

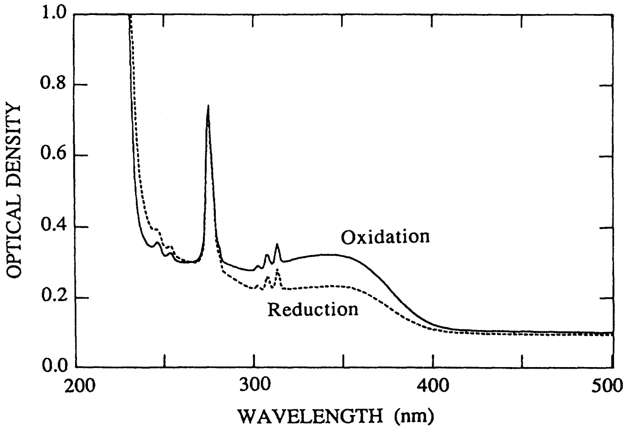

FIG. 2. Observed changes in the optical-absorption spectrum of GGG crystals after oxidation at 1173 K, and reduction at 1173 K.

C. Photoluminescence

In the as-received GGG crystals we observed luminescence from Cr^{3+} and Fe^{3+} impurity ions in the near-infrared region. The luminescence spectrum at 77 K with 275-nm excitation for the Fe^{3+} and Cr^{3+} ions is shown in Fig. 3. The emission spectra were taken beyond the range of correction of the spectrofluorimeter, and therefore were not corrected for the response of the pho-

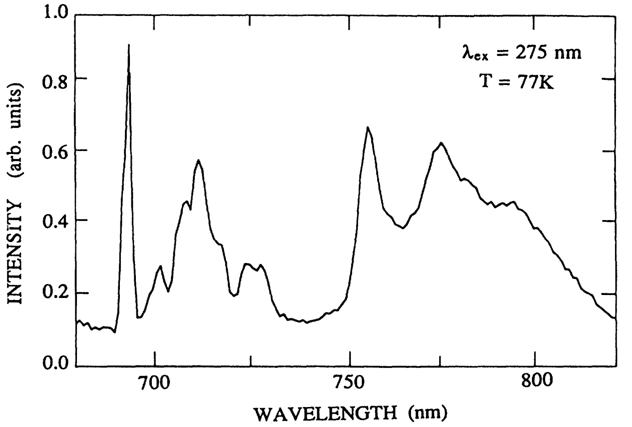

FIG. 3. Emission spectrum of Cr^{3+} (720 nm) and Fe^{3+} (800 nm) impurities at 77 K with 275-nm excitation.

tomultiplier tube. The excitation wavelength was chosen to correspond to both the Fe^{3+} charge-transfer band at 265 nm and the excitation of the chromium through the Gd$\rightarrow$Cr energy transfer. The chromium emission spectrum exhibited the sharp 695-nm emission-band characteristic of the $^2E \rightarrow {}^4A$ transition in a relatively high crystal field, along with the broad emission of the $^4T_1 \rightarrow {}^4A$ transition near 710 nm. The excitation spectrum of the *R*-line emission of Cr^{3+} showed a strong Gd-to-Cr energy transfer, as illustrated in Fig. 4. The upper curve shows the room-temperature absorption spectrum of a 0.5-mm-thick GGG crystal. The lower spectrum is the excitation spectrum for the Cr^{3+} emission at 695 nm. The excitation spectrum shows that there is evidence of significant energy transfer to the chromium from all the $4f$ levels of the Gd^{3+} ions. Further details of the observed energy transfer are reported elsewhere.[5] The emission spectrum of Fe^{3+} above 750 nm is very similar to previously observed emission spectra in YAG (yttrium aluminum garnet).[6] The presence of Fe impurities, as detected by the infrared luminescence, has some relevance to the optical absorption of the GGG crystals. The Fe^{3+} charge-transfer band at 265 nm should contribute to the ultraviolet absorption in these crystals. Oxidation and reduction of Fe impurities in YAG have shown that the intensity of the Fe^{3+} charge-transfer band increases under oxidation and decreases upon reduction.[7] However, the fact that the uv optical absorption near 265 nm shows a slight decrease under oxidation indicates that the Fe^{3+} charge-transfer band does not contribute significantly to the uv absorption in GGG.

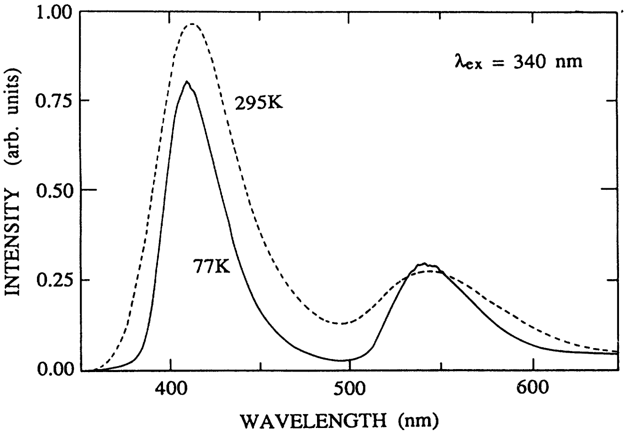

FIG. 5. Broad emission bands in GGG crystals from 340-nm excitation at room temperature and 77 K.

In addition to the infrared emission, the as-grown crystals of GGG exhibited several distinct emission bands in the visible spectrum. The emission spectra at room temperature and 77 K for 340-nm excitation are shown in Fig. 5. The visible fluorescence consisted of two broad bands, one centered at 415 nm and the second near 550 nm. Similar photoluminescence bands have been reported in neutron-irradiated YAG crystals. Oxidation and reduction treatments had a significant effect on the observed fluorescence properties of the crystal. Crystals that were oxidized at temperatures below 1273 K showed weaker emission at 550 and 415 nm when measured at room temperature. Following oxidation at temperatures above 1273 K, the emission from both of the bands was totally quenched. Reduction of the crystals at higher temperatures produced more intense emission from the 550- and 415-nm emission bands during excitation at 340 nm. Figure 6 shows a comparison of the visible emission bands for three reduction temperatures. The fluorescence intensities of both the 415- and 550-nm emission bands increase dramatically as the crystals are reduced at successively higher temperatures. The relative intensities of the photoluminescence bands did not maintain a constant ratio under successive reduction treatments, indicating that the photoluminescence bands are due to two distinct centers. The intensities of both photoluminescence bands increased as the 350-nm absorption band decreased. Apparently the color centers responsible for the photoluminescence bands are different from those that dominate the absorption in the ultraviolet region. It is clear that there are several defect centers that contribute to the

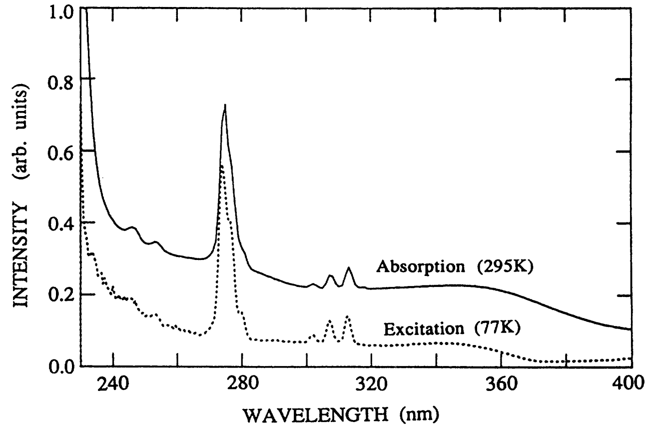

FIG. 4. Gadolinium-to-chromium energy transfer in GGG crystals. The top curve is the room-temperature absorption spectrum of a 0.5-mm-thick GGG crystal. The bottom curve is the excitation spectrum at 77 K of the Cr^{3+} emission at 695 nm.

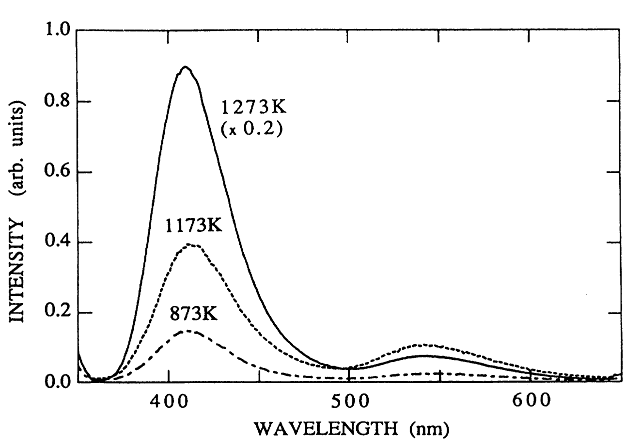

FIG. 6. Changes in intensity of the 415- and 550-nm emission bands following reduction at 873, 1173, and 1273 K.

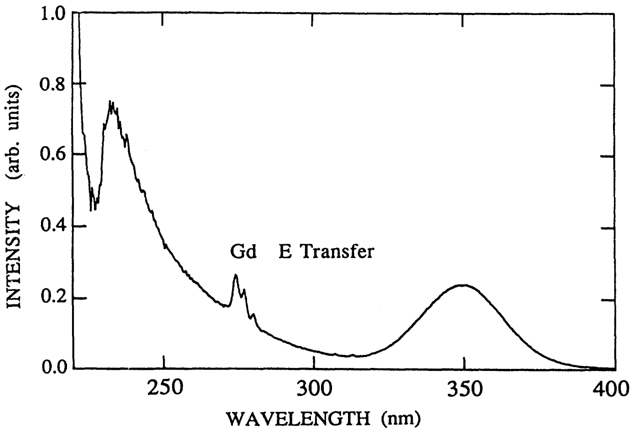

FIG. 7. Room-temperature excitation bands of the 550-nm emission band in GGG. The luminescence occurs from excitation at 340 and 240 nm as well as from energy transfer to the center from the Gd^{3+} ions at 275 and 310 nm.

color-center absorption bands in the ultraviolet region of the spectrum. We observed that the emission intensity at 415 and 550 nm decayed as a function of time under a constant intensity excitation source at 340 nm. Reduced samples, which were heated to 475 K and then excited at 340 nm, showed a decrease in emission intensity of 10–30 % after a 15-min excitation at room temperature.

The excitation spectrum for the 550-nm emission band is illustrated in Fig. 7. The excitation spectrum shows a peak near 350 nm, and an additional excitation band near 230 nm. In addition, there also is evidence of energy transfer from the Gd host ions to the luminescence center, as indicated by the peaks near 275 nm which correspond to the excitation of the Gd^{3+} transitions. The excitation spectrum of the 550-nm emission is anomalous in that the ratio of the 230- and 350-nm excitation bands does not remain constant but varies as a function of the reduction temperature of the sample. Furthermore, emission spectra suggested that multiple types of centers contributed to the 550-nm emission. Figure 8 shows the change in the observed emission band as the excitation wavelength was scanned from 320 to 340 nm. As the excitation wavelength decreases, the emission band shifts further to the red. By comparison, the 415-nm emission band did not shift appreciably over the same excitation region. Our results suggest that the 550-nm emission band is composed of similar types of perturbed centers, which give rise to the inhomogeneous broadening of both the 550-nm emission band and 350-nm excitation band in samples of reduced GGG.

D. γ-ray and ultraviolet irradiation

While the changes in the two emission bands following oxidation and reduction did not seem to be correlated with the changes observed in the optical-absorption spectrum, the optical-absorption bands in the near uv region were linked to the observed coloration of the crystal in the visible region following uv or γ-ray irradiation. Understanding these coloration effects is of principal concern for laser materials that may be used for space-based remote-sensor applications or flashlamp pumped lasers.

Irradiation with γ rays from a ^{60}Co source or excitation with ultraviolet light in the absorption band at 350 nm resulted in the visible coloration of our GGG samples. The excitation was carried out using a 1000-W xenon lamp in conjunction with a 0.1-m monochromator. The spectral characteristics of the visible absorption induced by γ-ray or uv irradiation were similar in the as-received crystals and samples which were oxidized or reduced at temperatures below 1300 K. Characteristic absorption spectra for the as-grown, uv-, and γ-ray-irradiated crystals are shown in Fig. 9. The color centers produced by the irradiation resulted in a net increase in absorbance from 700 nm to the band edge of the crystal. The absorption in the visible region peaked near 450 nm. The γ-ray irradiation produced the same effect as the uv excitation except that the increase in absorbance was higher. Crystals that were oxidized showed an increase in the visible absorption following the irradiation. Crystals that had been reduced were more resistant to the coloration effects of the γ-ray irradiation. In all our sam-

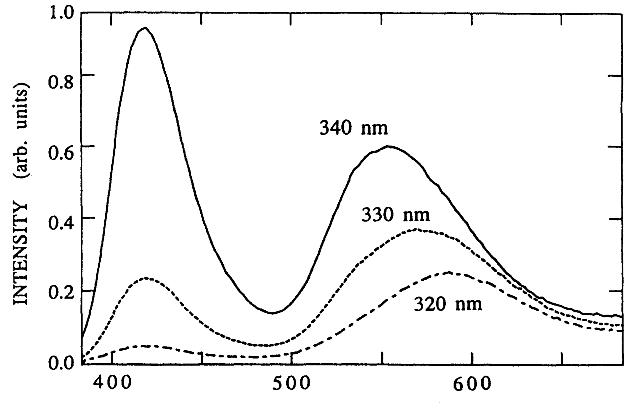

FIG. 8. Spectral dependence of the 550-nm emission band following excitation at 340, 330, and 320 nm.

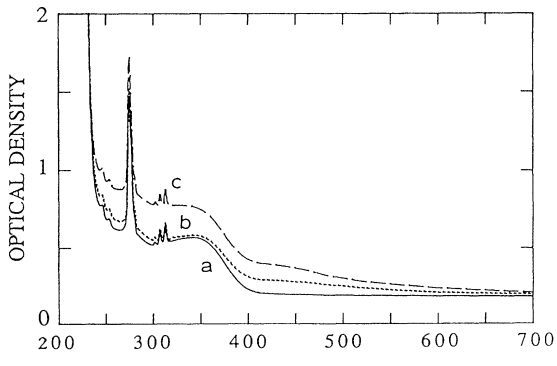

FIG. 9. The absorption spectrum of a 0.5-mm-thick GGG crystal (a) as-grown, (b) following uv exposure, and (c) after γ-ray irradiation.

ples, the intensity of the visible coloration following γ-ray or uv irradiation was correlated with the intensity of the 350-nm color-center absorption band prior to the irradiation. The visible coloration produced by the irradiation exhibited a photochromic effect in that it could be reversed by illumination with visible light.

The visible absorption bands could also be removed by thermal annealing at temperatures near 500 K. Heating the samples after irradiation produced a thermoluminescence whose spectra characteristics were a function of the prior sample treatment. Samples that had been reduced prior to γ-ray or uv irradiation exhibited a strong yellow thermoluminescence at approximately 350 K and a weaker red luminescence at a temperature near 500 K. The thermoluminescence is thought to arise from the 540-nm color-center emission for the low-temperature glow peak, and from Cr^{3+} for the high-temperature peak. Crystals which had been oxidized, and therefore did not show the 540-nm photoluminescence, also did not exhibit the yellow thermoluminescence band following irradiation.

The results of the γ-ray and uv irradiations indicate that the 350-nm absorption band serves as a source of ionizable centers that can result in the release of charge carriers and subsequent retrapping at alternate sites. Therefore, the degree of coloration after uv irradiation was dependent on the number of centers associated with the 350-nm absorption band. As a consequence, the crystals that were subjected to oxidation at $T < 900\,^{\circ}\mathrm{C}$ were more strongly colored following uv or γ-ray irradiation than their reduced counterparts.

E. Neutron-irradiated crystals

In addition to the intrinsic defects in GGG crystals, other types of color centers can be produced by neutron irradiation. Crystals of GGG were irradiated at the Oak Ridge National Laboratory, National Low Temperature Neutron Irradiation Facility, with a cumulative neutron dose of 2×10^{17} and 1×10^{18} neutrons/cm^2 (n/cm^2). The samples were cooled with flowing helium gas and the ambient temperature was approximately 320 K. The absorption spectrum for a 0.5-mm-thick crystal irradiated with 2×10^{17} n/cm^2 is illustrated in Fig. 10. The changes in the absorption throughout the visible spectrum were similar to that observed for γ-ray-irradiated crystals. There were, however, pronounced changes in the absorption from 380 nm to the absorption edge of the crystal. This shift in the band edge to lower energy has been linked to partial nonstoichiometry in the GGG crystals.[8] Annealing of the samples to 800 K eliminated most of the absorption caused by the neutron irradiation, but some absorption below 250 nm remained, indicating the existence of additional stable defects in the crystal. Excitation near the band edge in the irradiated crystals produced a weak broad emission band at 490 nm which was not observed in any of the as-grown, oxidized, reduced,

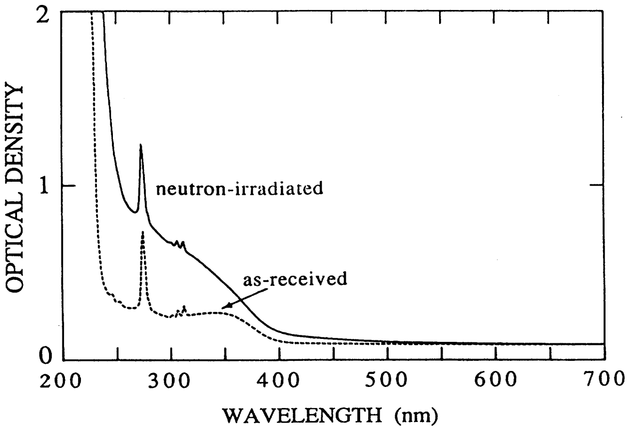

FIG. 10. Absorption spectrum of a 0.5-mm-thick crystal of GGG following neutron irradiation of 2×10^{17} neutrons/cm^2. The absorption spectrum of an unirradiated sample is given, as a reference, by the dotted line.

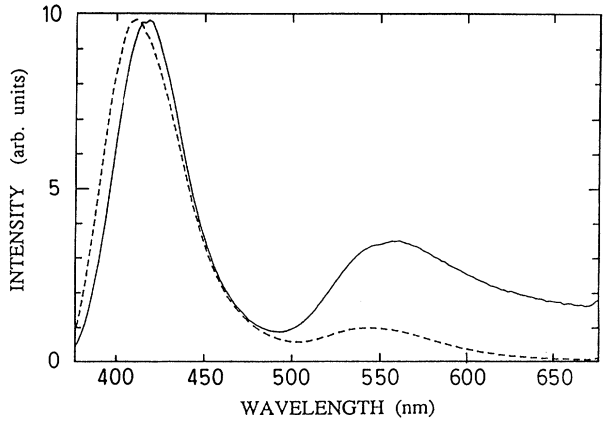

FIG. 11. Room-temperature emission spectrum of a neutron-irradiated GGG crystal excited with 350-nm light. The crystal was irradiated with a dose of 1×10^{18} neutrons/cm^2. The dashed curve shows the emission spectrum of a reduced GGG crystal for comparison.

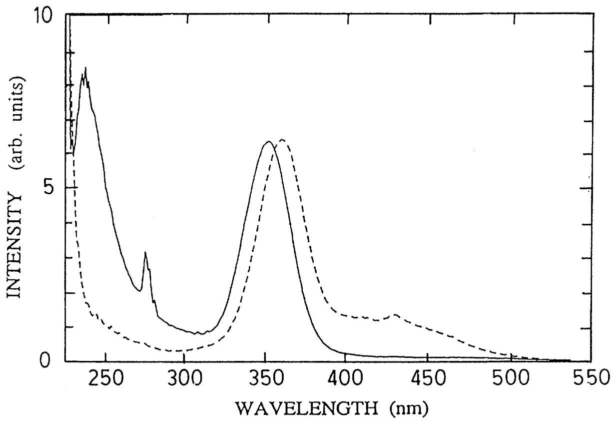

FIG. 12. Room-temperature excitation spectrum of the 550-nm emission band in reduced GGG (solid curve), and a GGG crystal irradiated with 1×10^{18} neutrons/cm^2. The detector monitored the emission at 560 nm.

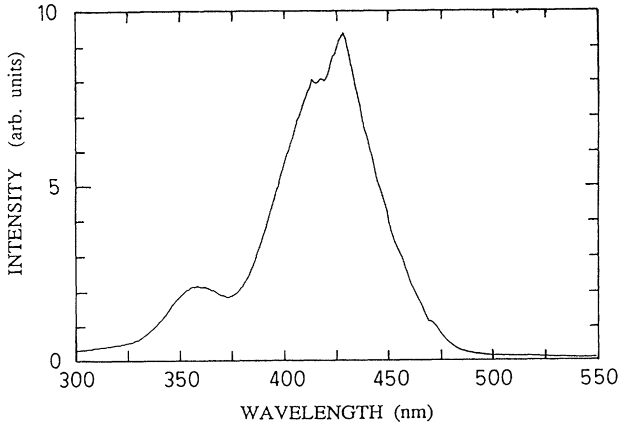

FIG. 13. Excitation spectrum at 77 K of the 550-nm emission band in a GGG crystal irradiated with 1×10^{18} neutrons/cm^2. The detector monitored the emission at 560 nm.

or γ-ray-irradiated crystals. We observed a factor of 5 increase in the strength of the 490-nm emission as the sample was cooled from 300 to 77 K. An excitation spectrum of the 490-nm emission band showed a single broad peak near 230 nm. This band may be responsible for the observed shift in the band edge of the neutron-irradiated crystals.

Neutron-irradiated crystals also showed some of the same photoluminescence bands as the reduced GGG crystals. The photoluminescence bands were extremely weak in crystals irradiated with 2×10^{17} n/cm^2, but were considerably stronger in the crystals irradiated at 1×10^{18} n/cm^2. The emission band for the higher-dose neutron-irradiated GGG crystal is shown in Fig. 11, along with the emission spectra in a reduced GGG sample for comparison. The emission spectra have been normalized to the peak of the 415-nm emission band. We believe that the shift of the 415-nm emission peak in the irradiated GGG crystal is due to self-absorption in the crystal. For crystals irradiated at a dose of 1×10^{18} n/cm^2, the absorption coefficient at 375 nm was approximately 35 cm^{-1} and doubled to 70 cm^{-1} at 350 nm. The excitation spectra of neutron-irradiated and reduced GGG crystals are shown in Fig. 12. Again, there was a similar excitation peak near 350 nm in both samples. The shift to lower energy in the neutron-irradiated crystal again is likely due to the effects of the strongly changing absorption coefficient below 400 nm. The extremely high absorption coefficient of the irradiated crystal below 300 nm also accounts for the absence of the Gd energy-transfer peaks and the 230-nm excitation band. The heavily neutron-irradiated crystal also showed an excitation peak for the 550-nm emission band at 430 nm that was absent in the reduced crystals. This excitation peak at 430 nm was dramatically enhanced by cooling the sample to 77 K. Figure 13 shows that the low-temperature excitation peak at 430 nm is much stronger than the 350-nm excitation band that dominated the room-temperature excitation spectrum.

III. DISCUSSION

We have examined the optical properties of color centers in as-grown GGG crystals as well as color centers produced by oxidation and reduction and by neutron irradiation. It is clear from the results of our experiments that the color centers that are primarily responsible for the uv absorption bands in GGG crystals are distinct from the color centers that give rise to the photoluminescence bands, in spite of the fact that photoluminescence bands also absorb in the same spectral region. The uv absorption spectrum near the band edge consisted of at least two absorption bands, located near 250 and 350 nm. Under oxidation and reduction, these two absorption bands show complementary properties. The color centers that produced these absorption bands occur as a consequence of the addition of small amounts of Ca^{2+} during crystal growth and serve as charge compensators in the GGG crystals. Oxygen vacancies would be prime candidates as charge compensators; however, on the basis of results from the oxidation and reduction experiments, it appears that simple oxygen vacancies are not responsible for the 350-nm absorption band in GGG. The failure to diminish the 350-nm absorption band following high-temperature oxidation argues against the contention that this color center is a simple oxygen vacancy center. The annealing in oxygen of YAG crystals at these high temperatures has shown a decrease in the concentration of anion vacancy defects,[9] and we expect this to hold true in GGG crystals as well. However, we cannot rule out the possibility that some component of the 250-nm absorption is related to oxygen vacancy centers. The absorption of GGG crystals in this region does show similar features to YAG under oxidation.[9]

It is possible that both oxygen vacancy centers and various trapped-hole centers are responsible for the uv absorption bands in GGG crystals. Both of these types of centers have high oscillator strengths and would also serve as charge compensators for the Ca^{2+} impurities. Trapped-hole centers (O$^-$ ions trapped at cation vacancies or impurity sites) have been identified in YAG crystals, and the trapped-hole centers in YAG absorb over the same spectral region as the color centers in GGG crystals.[10,11]

Ultraviolet and γ-ray irradiation of the GGG crystals results in visible coloration of the samples. The degree of coloration following uv excitation or γ-ray irradiation is dependent upon the intensity of the 350-nm color-center absorption band. Presumably, the visible coloration results from the release of charge carriers from the color center associated with the 350-nm absorption band. Previous measurements of photoconductivity in GGG crystals show an onset of a strong photoconductivity band in this spectral region.[12] Release of these charge carriers, and their subsequent retrapping, produces changes in the absorption spectrum upon exposure to uv light or γ-ray irradiation. Therefore, oxidation of the samples increases the strength of the 350-nm absorption band and also enhances the coloration in the visible spectrum upon exposure to uv light. Optical or thermal bleaching of the brown crystals removes the coloration and returns the crystal to the transparent state. Annealing of the samples in a reducing atmosphere greatly reduces the coloration under uv or γ-ray irradiation. In this regard, our results are similar to previous investigations of GGG crystals that were not doped with calcium.[13] However, γ-ray irradiation of reduced GGG crystals results in a larger increase in absorption for wavelengths less than 300 nm than in their oxidized counterparts.

A possible mechanism, which could account for the general absorption properties of the GGG crystals, is that the addition of Ca introduces oxygen vacancies and trapped-hole centers to charge compensate the aliovalent impurities. Oxidation and reduction experiments indicate that the 350-nm absorption band is likely due to trapped-hole centers, possibly as O^- centers trapped at Ca impurity sites. Color centers associated with oxygen vacancies may dominate the absorption at shorter wavelengths. Optical excitation at 350 nm may cause the holes to migrate and trap at other sites producing other species of trapped-hole centers, or excitation of the trapped-hole center may form O_2^{2-} centers and centers associated with electron traps. If oxygen vacancies are present in the crystal, they should form electron traps and produce F^+ centers upon exposure to ionizing radiation. We have not been able to identify any of the color-center absorption bands with transitions of the F^+ center. The energy levels of the F^+ center vary widely in oxide hosts. In YAG, three broad optical-absorption bands at 800, 450, and 350 nm have been identified as transitions of the F^+ center.[10,14] However, the F^+ center in YAG is unstable at room temperature. If the F^+ center exists in GGG, it also may be unstable at room temperature.

One difficulty with the above model is that results of a previous investigation appear to conflict with some aspects of our assignment. Metselaar *et al.* have investigated the coloration of GGG crystals doped with Eu^{3+} and Tb^{3+}.[13] Exposure of these doped crystals to uv irradiation resulted in a similar coloration to that observed in our experiments. However, the Tb-doped crystals were much more susceptible to coloration following uv exposure than the Eu-doped crystals. They argued that since Eu^{3+} serves as an electron trap and Tb^{3+} as a hole trap, the resistance to coloration of the Eu-doped sample indicated that the color centers were due to electron-trap centers. In comparing our results to this previous work, we point out that (i) the Tb and Eu concentrations were approximately two orders of magnitude larger than the Ca dopant concentration in our crystals, even though the coloration after uv exposure was comparable in the two cases, and (ii) the absorption spectrum of the Eu and Tb samples before irradiation shows no evidence of the 350-nm absorption band which was so prominent in our GGG crystals. Since it appears that there are a number of different types of color centers that absorb at wavelengths less than 350 nm, it may be that completely different mechanisms are responsible for the coloration in these two cases. The absorption spectrum of neutron-irradiated crystals confirms the fact that there are many color centers whose absorption bands are concentrated in the spectral region from 350 nm to the band edge. In this respect, GGG differs from YAG in that neutron-irradiated YAG crystals have absorption bands that cover the entire spectral region from the uv band edge to the infrared.[15,16]

The existence of a wide variety of color centers in GGG is responsible for the complex photoluminescence properties of the crystals. We have identified luminescence from both Cr^{3+} and Fe^{3+}, through direct excitation and energy transfer from Gd^{3+} ions. There are two broad photoluminescence bands near 420 and 550 nm. Both of these emission bands are enhanced by annealing the crystal in a reducing atmosphere, and both have a broad excitation band near 350 nm. Since the intensities of these luminescence bands increase as the 350-nm color-center absorption band decreases, we have concluded that the center that produced the 350-nm absorption band is independent of the center responsible for the photoluminescence. Consequently, we can say little about the nature of the centers that produce the luminescence bands. The 420-nm emission band in GGG is similar in both energy and bandwidth to a luminescent center in YAG.[15] Therefore we believe that the center responsible for the 420-nm emission is due to an intrinsic defect on the oxygen sublattice of the garnet crystals.

The 550-nm emission band in GGG is also similar to a luminescence band in YAG. An emission band which peaks at 570 nm in Mn-doped YAG crystals has been investigated by Bernhardt and identified as Mn^{2+} emission.[17,18] We have examined emission in neutron-irradiated YAG crystals and found an emission band with similar characteristics to the emission band cited by Bernhardt. While the emission band is similar in energy to Mn-emission YAG, the excitation spectrum could vary widely for the two hosts. This is in part due to the fact that the transitions on Mn^{2+} are highly forbidden so that luminescence occurs as a result of the interaction with defects in the host lattice. While Mn^{2+} impurities may be responsible for the 550-nm emission, a determination cannot be made on the basis of our experiments. If the 550-nm emission in GGG is due to Mn^{2+} impurities, then there must be a variety of similar centers in order to account for the inhomogeneous broadening of both the 550-nm emission band and the 350-nm excitation band.

IV. SUMMARY

In summary, we have investigated the nature of color centers in GGG crystals that occur as a consequence of the addition of Ca during crystal growth, and are produced by irradiation. It is apparent that a wide variety of color centers, which all absorb at similar wavelengths, are present in the GGG crystals. These intrinsic color centers may be photoionized during uv excitation, which can occur during flashlamp pumping of GGG laser host materials. The subsequent trapping of the photoionized charge carriers results in broad visible absorption bands that act as parasitic absorption centers for laser transitions. The changes in the optical properties of the material under uv excitation illustrates that the presence of color centers in laser host materials can be detrimental even though they appear to lie mainly outside the spectral region of laser transitions. The dynamical processes that occur in the color centers during optical excitation may result in efficient loss mechanisms that are not apparent from the optical-absorption spectrum. Our experimental results suggest that stabilization of large-diameter crystals by the addition of Ca may seriously degrade the laser performance of gadolinium garnet hosts.

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