Effect of air annealing on the spectral properties of Ce:Y₃Al₅O₁₂ single crystals grown by the temperature gradient technique

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Abstract

Five absorption bands, at 227, 300, 340, 370 and 457 nm, were observed in the optical absorption spectrum of Ce:Y₃Al₅O₁₂ (Ce:YAG) crystals grown by the temperature gradient technique (TGT). The absorption bands at 227, 340, and 457 nm were identified as belonging to the Ce³⁺-ion in the YAG crystal. A near UV optical emission band at 398 nm was observed, with an excitation spectrum containing two bands, at 235 and 370 nm. No fluorescence was detected under 300 nm excitation. The pair of absorption bands at 235 and 370 nm and the absorption band at 300 nm were attributed to the F- and F⁺-type color centers, respectively. The color centers model was also applied to explain the spectral changes in the Ce:YAG (TGT) crystal, including the reduction in the Ce³⁺-ion absorption intensity, after annealing in an oxidizing atmosphere (air).

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1. Introduction

Ce³⁺-doped yttrium–aluminum garnet crystals, Y₃Al₅O₁₂ (Ce:YAG), are well-established scintillators which show extremely high mechanical and chemical stability, high light yield and short
luminescence decay of about 60 ns [1–4]. Their dominant green emission at 550 nm fits well the spectral sensitivity dependence of Si photodiodes and CCD detectors. All these properties suggest that the Ce:YAG scintillator can be successfully employed in various fields, mainly for the detection of light charged particles and high-count-rate applications [5,6].

At present, Ce:YAG scintillation crystals are mainly grown by the Czochralski method (CZ) [6]. Recently, we have reported on the growth of Ce:YAG crystal with a diameter of 76 mm by the temperature gradient technique (TGT) [7]. In this work, we investigate the optical properties of both TGT- and CZ-grown Ce:YAG and present new details on the optical absorption and emission of these crystals associated with color centers.

2. Experimental procedure

Ce:YAG single crystals were grown both by the TGT and the CZ methods. Detailed information about the Ce:YAG growth by TGT can be found in our previous work [7]. In the CZ process, the raw materials including highly pure oxide powders, Y2O3, CeO2, and Al2O3, were the same as those used in the TGT. The growth apparatus was described elsewhere [8] and the atmosphere in the furnace was high-purity nitrogen. Two Ce:YAG samples were prepared, one denoted as Ce:YAG (TGT) and the other—Ce:YAG (CZ). These two samples were perpendicular to the [111] growth axis and their thickness was about 0.4 mm after polishing. With regard to the as-grown Ce:YAG (TGT), we initially measured its absorption and fluorescence spectra, then it was annealed in air at 1200 °C for 12 h.

Absorption spectra and fluorescence spectra were measured using a V-570-type ultraviolet/visible/near-IR spectrophotometer and FP-6500/6600 fluorescence spectrometer made by Japan JASCO Company, respectively. The wavelength range of the absorption spectra measurements was 190–1200 nm; the light sources were a deuterium lamp (190–350 nm) and a halogen lamp (340–1200 nm), and the spectral resolution was 1 nm. For fluorescence spectra measurements, the light source for excitation was a xenon lamp, the wavelength range was 220–750 nm, the spectral resolution was 1 nm and the slit sizes for both the excitation and fluorescence light were 3 nm. All measurements were performed at room temperature.

3. Results and discussion

Three similar absorption peaks at about 227, 340, and 457 nm have been observed for as-grown Ce:YAG (TGT) and as-grown Ce:YAG (CZ) as shown in Fig. 1. These absorption peaks are attributed to the absorption of Ce3+-ions in YAG crystal [9,10]. Two additional absorption peaks at 300 and 370 nm are observed in the absorption spectrum of the as-grown Ce:YAG (TGT), and they do not appear in the absorption spectrum of the as-grown Ce:YAG (CZ). These two absorption peaks are presumably associated with the absorption of certain color centers in the as-grown Ce:YAG (TGT), but the character of the color centers needs further study.

The excitation and emission spectra of Ce3+ in the as-grown Ce:YAG (TGT) are shown in Fig. 2. The excitation and emission spectra of Ce3+ in the as-grown Ce:YAG (CZ) are nearly identical with Fig. 2. In contrast, the response to optical excitation within the absorption bands attributed to color centers is different for the two types of

![Absorption coefficient (cm⁻¹) vs. Wavelength (nm)](image)

Fig. 1. RT absorption spectra of as-grown Ce:YAG single crystals grown by CZ (1) and TGT (2).
crystals. For the as-grown Ce:YAG (TGT) sample, under 300 nm excitation, no luminescence was detected; under 370 nm excitation, the emission at 398 nm was detected. The excitation spectrum was measured for the 398 nm emission, and the excitation peaks at 235 and 370 nm were observed as shown in Fig. 3. In the as-grown Ce:YAG (CZ) sample, no luminescence can be detected under 300 or 370 nm excitation.

Yin et al. [11] and Kurtz [12] have attributed the absorption peak at 370 nm to the absorption of F-type center perturbed by Yb$^{2+}$ in the YAG host. Both Wu et al. [13] and Yan et al. [14] have observed the absorption peak at 370 nm in absorption spectra of YAG crystals grown by CZ in deoxidized atmosphere, while Yan et al. have attributed this peak to absorption by an F-type color center. The 370 nm absorption peak has been observed also in a gamma-irradiated YAG crystal grown by CZ and attributed to the F-type color center as well [15].

We recall that the 398 nm emission of the Ce:YAG (TGT) sample is excited only within the 370 and 235 nm peaks (Fig. 3). This implies that the absorption bands at 300 and 370 nm must be attributed to different color centers. However, both color centers are most probably of the F-type (electrons trapped at oxygen vacancies). In the crystal growth process of TGT, a mild deoxidizing atmosphere exists in the furnace because of adopting graphite resistance as a heater and using high-purity purging Ar gas in the furnace, so that O$^{2-}$ ions vacancies can be produced in the crystal during the growth process. These O$^{2-}$ vacancies can trap electrons and became F-type centers (F, F$^+$, etc.). The F-type color centers are difficult to produce in the CZ crystal growth process when an inert (nitrogen) atmosphere exists in the furnace [16].

In proof of the above, an as-grown Ce:YAG (TGT) sample has been annealed in air at 1200 °C for 12 h and we have compared the absorption and the fluorescence spectra of Ce:YAG (TGT) before and after air anealing. The fluorescence spectra of Ce$^{3+}$ remain unchanged, but no emission is detected under 300 or 370 nm excitation. The absorption peaks at 300 and 370 nm disappear after air annealing as shown in Fig. 4 and the overall intensity of absorption peaks of Ce$^{3+}$ decreases. A difference absorption spectrum has been deduced to characterize the changes in the concentrations of the color centers and Ce$^{3+}$-ions in Ce:YAG (TGT) before and after air annealing.

The difference absorption coefficient at 190–540 nm is below zero, and four negative difference absorption peaks at 235, 300, 370, and 458 nm are clearly observed as shown in Fig. 5. The absorption peak at 457 nm belongs to the absorption of Ce$^{3+}$ in YAG host as shown in Fig. 1. Therefore, the negative difference absorption peak at 458 nm indicates that the concentration of Ce$^{3+}$ in YAG decreases after air annealing. We recall (Fig. 3) that an excitation peak at 235 nm
is also observed for 398 nm emission. The corresponding absorption peak at 235 nm is only vaguely seen in the absorption spectrum of as-grown Ce:YAG (TGT), as shown in Fig. 1, since it is very weak and is overlapped with the 227 nm absorption peak of Ce$^{3+}$. We conclude, therefore, that the excitation peaks at 235 and 370 nm shown in Fig. 3 belong to an identical F-type color center, while the absorption peak at 300 nm (Fig. 1) is attributed to another kind of F-type color center. This color centers model can be applied to explain the spectra changes of Ce:YAG (TGT) before and after air annealing.

During the air annealing process, oxygen atoms can diffuse into the crystal to some extent and decrease the concentration of oxygen vacancies of [17]. Furthermore, the Ce$^{3+}$-ion can easily lose an electron and become a Ce$^{4+}$-ion [18]. Thus, the following reactions can be expected:

$$F \text{ (two electrons trapped at an oxygen ion vacancy)} + O = O^{2-}; \ F^+ \text{ (one electron trapped at an oxygen ion vacancy)} + Ce^{3+} + O = Ce^{4+} + O^{2-}.$$  

As a result, after air annealing, the absorption peak of F-type color centers disappears and the absorption intensity of Ce$^{3+}$ in Ce:YAG (TGT) obviously decreases as shown in Figs. 4 and 5. Consequently, the emission at 398 nm cannot be detected again under 235 or 370 nm excitation, which is confirmed by the experiment.

### 4. Conclusions

Relatively weak absorption peaks at 300 and 370 nm have been observed in the as-grown Ce:YAG (TGT) crystals and attributed to different F-type color centers. Optical excitation at 370 nm gives rise to emission of light peaking at 398 nm, yet no fluorescence is detected below 300 nm excitation. In addition to the 370 nm band, the excitation spectrum of the 398 nm emission also contains a band peaking at 235 nm. The latter can be hardly resolved in the absorption spectrum due to an overlap with the 227 nm absorption band of the Ce$^{3+}$-ion, but it appears in the difference absorption spectrum of Ce:YAG (TGT) before and after air annealing. The absorption at 235 and 370 nm and the corresponding emission at 398 nm disappear after annealing in air, and these bands are attributed to an F-type color center. The absorption at 300 nm, also disappear after air annealing followed by a reduction in the intensity of Ce$^{3+}$-ion absorption bands, is attributed to an F$^+$-type color center. The color centers model invoked to explain the spectral changes in Ce:YAG (TGT) before and after air annealing is clearly qualitative in nature, and other studies (electron spin resonance, thermoluminescence, etc.) have to be carried out to

![RT absorption spectra of Ce:YAG (TGT) before and after air annealing.](image1)

![Difference absorption coefficient of air-annealed versus as-grown Ce:YAG (TGT) crystal.](image2)
confirm it and to obtain quantitative estimates of the concentrations of defects involved.

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References