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Study of Blue Photoluminescence in Titanium Doped Al_2O_3 Single-Crystals

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Abstract. Optical properties have been investigated in titanium doped sapphire, prepared under oxidized condition. Charge-transfer transitions to $3d$ states of tetravalent Ti^{4+} from $2p$ ones of O^{2-} are found to be located below the fundamental absorption edge of Al_2O_3 . The photo-excitation for this band leads to the intense blue emission, the spectrum of which is quite different from the luminescence of the $d-d$ transitions in trivalent Ti^{3+} . The UV-irradiation also leads to an absorption peak below the charge-transfer band, resulted from that the photo-excited electrons in part form color centers. The post-annealing at higher temperatures above 300°C completely destroys the color centers. The blue photoluminescence is found to be greatly suppressed by the UV-irradiation and is recovered by the post-annealing. This fact indicates that the color centers prevent the blue emission.

1. Introduction

Titanium doped sapphire ($\text{Ti-Al}_2\text{O}_3$) is a textbook material for wavelength tunable lasers [1]. $\text{Ti-Al}_2\text{O}_3$ exhibits the intense photoluminescence near infrared region, originated from $d-d$ transitions of trivalent Ti^{3+} ions. In addition to this red emission, a broad photoluminescence is observed at around 400 nm under UV irradiation [2]. The blue luminescence was ascribed to emission from tetravalent Ti^{4+} ions [3], due to $4s-3d$ transition of Ti^{3+} ions [4], related to charge-transfer excitations from $2p$ states of O^{2-} to $3d$ ones of Ti^{4+} [5, 6], or transitions associated with F^+ centers [7].

Recently, the blue emission of $\text{Ti-Al}_2\text{O}_3$ has been intensively studied for X-ray scintillation detector [8, 9]. Although there have been many reports for the blue emission of $\text{Ti-Al}_2\text{O}_3$, the origin remains unclear. To consider this problem, we have studied the UV irradiation effects on the optical properties of both ceramics and single-crystals of $\text{Ti-Al}_2\text{O}_3$, prepared in oxidized atmosphere.

2. Experimental

Ceramics samples of oxidized $\text{Ti-Al}_2\text{O}_3$ were synthesized by solid-state reaction. Appropriate amount of Al_2O_3 and TiO_2 powders was well mixed and pressed into a rod shape. The rods were sintered in air at 1500°C for 24 hours. Single-crystals of oxidized $\text{Ti-Al}_2\text{O}_3$ were melt-grown by a floating-zone method in O_2 atmosphere. Concentration of Ti was 0.05 mol%. The powder diffraction patterns of all samples agree well with those of Al_2O_3 . The sample preparation in detail will be described elsewhere.

UV irradiation was carried out in air at room temperature. A conventional mercury lamp with the wavelength of 254 nm and the power density of $44\mu\text{W}/\text{cm}^2$ on the sample was used. The irradiation was done for 24 hours. Post-annealing of the samples was carried out in air for 24 hours with using the

conventional electric furnace. The optical transmission spectrum was measured by JASCO V-550 spectrometer, and the photoluminescence and photoluminescence excitation spectra were analyzed by HITACHI F-4500 spectrometer.

3. Results and Discussions

3.1. Optical properties of oxidized $\text{Ti-Al}_2\text{O}_3$

Optical properties of oxidized $\text{Ti-Al}_2\text{O}_3$ are quite different from those of conventional $\text{Ti-Al}_2\text{O}_3$ prepared in reduced atmosphere. The former is colorless, and the latter is pink. The transmission spectrum of the as-grown single-crystal of oxidized $\text{Ti-Al}_2\text{O}_3$ is shown in figure 1. The thickness of the sample is about 2 mm. Here the spectrum of nominally pure Al_2O_3 is also plotted for comparison. We immediately find that the oxidized $\text{Ti-Al}_2\text{O}_3$ exhibits a striking absorption below the fundamental absorption edge ~ 130 nm of Al_2O_3 . On the other hand, no significant absorption at around 500 nm, characteristics of the $d-d$ transitions in trivalent Ti^{3+} ions, is observed. Therefore, the absorption band at around 250 nm should be associated with tetravalent Ti^{4+} ions. Namely, the absorption band is originated from the charge-transfer excitations from $2p$ states of O^{2-} to $3d$ ones of Ti^{4+} .

Under photo-excitation on the charge-transfer band, both the single-crystalline and ceramics samples of oxidized $\text{Ti-Al}_2\text{O}_3$ exhibit the intense blue emission. Figure 2 displays the photoluminescence spectra of the single-crystals, where the wavelength of the excitation is 254 nm. We find the blue photoluminescence peaking at about 420 nm and ranging between 300 nm and 600 nm. The photoluminescence excitation spectrum reveals that the blue emission occurs for the excitation wavelength between 200 nm and 280 nm. This wavelength range is in good agreement with the charge-transfer band observed in absorption spectrum. Therefore, the blue emission should be related to tetravalent Ti^{4+} ions, not to trivalent Ti^{3+} ones. Indeed, the red luminescence, characteristics of Ti^{3+} [1], is found to be very weak in oxidized $\text{Ti-Al}_2\text{O}_3$.

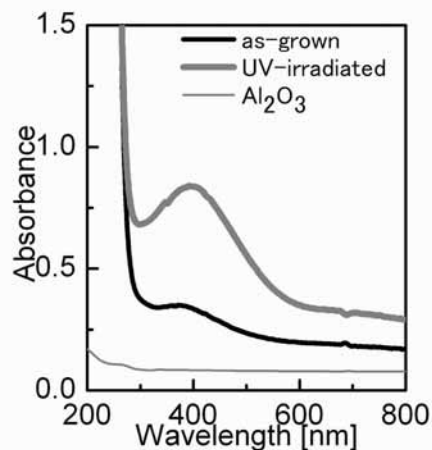


Figure 1. Absorption spectrum of an as-grown single-crystal of oxidized $\text{Ti-Al}_2\text{O}_3$. The spectra of Al_2O_3 and UV-irradiated $\text{Ti-Al}_2\text{O}_3$ are also shown.

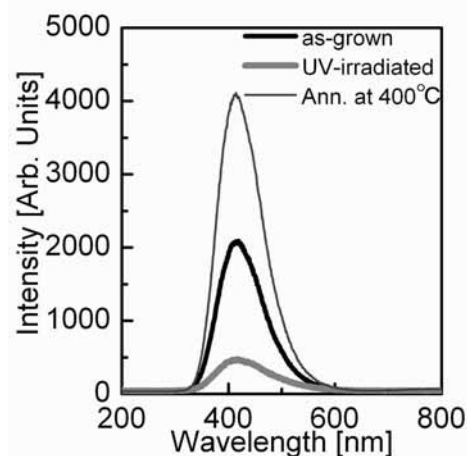


Figure 2. Photoluminescence of as-grown, UV-irradiated and post-annealed single-crystals of $\text{Ti-Al}_2\text{O}_3$. The spectra are excited at 254 nm.

3.2. Effects of UV irradiation on the absorption spectrum

As can be seen in figure 1, the absorption at around 400 nm is strikingly increased by the UV-irradiation. The 400 nm band is rather broad and, thereby, blue and green components of incident light are reduced. Actually, after the UV-irradiation the sample becomes yellow. Since no color change is

observed for 365 nm irradiation, the photo-excited carriers on the charge-transfer band are partly trapped and, then, the color centers are created [7].

Figure 3 illustrates the absorption spectra of the post-annealed single-crystals. Evidently, the 400 nm peak can be suppressed by annealing. To consider the annealing effect in detail, the absorbance ΔAbs due to the color centers is estimated using the relation $\Delta Abs = Abs - Abs_{BG}$, where Abs is the absorbance at 400 nm and the value at 600 nm is employed as the background Abs_{BG} . Figure 4 shows the dependence of ΔAbs on annealing temperature. The destruction of the color centers is complete at about 400°C.

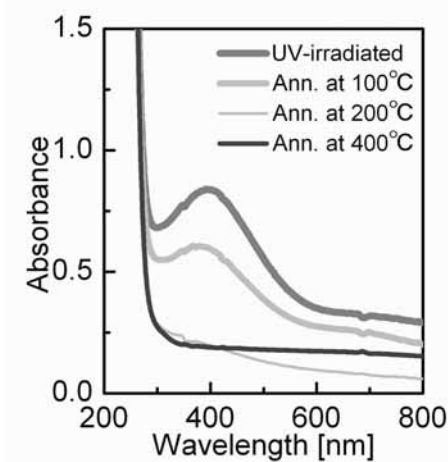


Figure 3. Absorption spectra of Ti-Al₂O₃ single-crystal annealed at several temperatures.

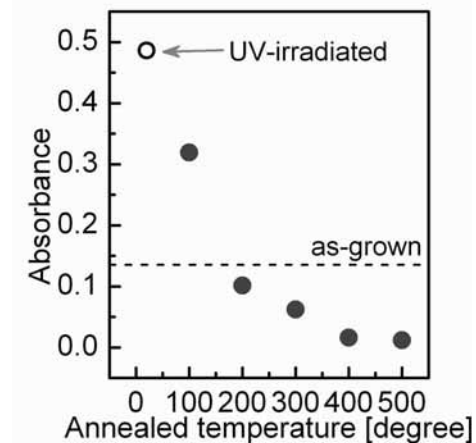


Figure 4. Absorbance at 400 nm as a function of annealed temperature, where the background is subtracted.

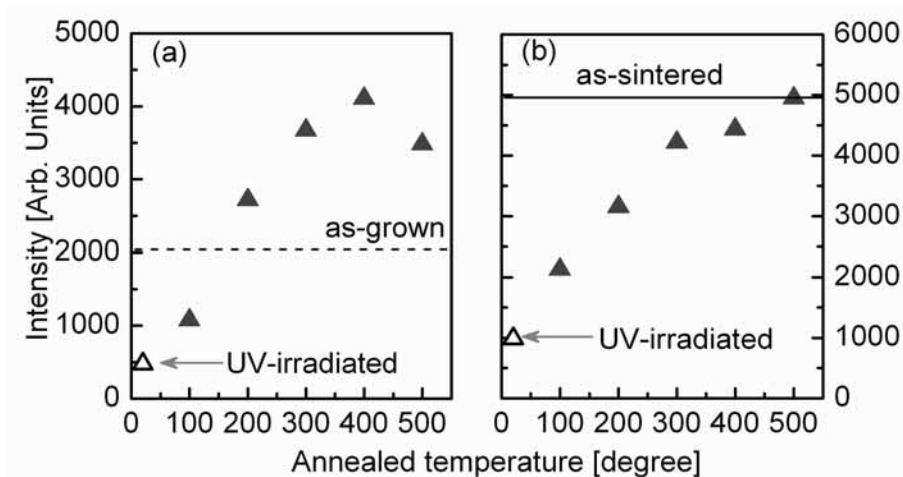


Figure 5. Photoluminescence intensity of (a) Ti-Al₂O₃ single-crystal and (b) ceramics as a function of annealed temperature.

3.3. Effects of UV irradiation on the photoluminescence spectrum

As shown in figure 2, the blue emission is remarkably reduced by the UV-irradiation and enhanced by the post-annealing. In figure 5 the peak intensity of the blue emission is plotted as a function of annealed temperature, where the results of the ceramics samples are also shown. The intensity abruptly increases at temperatures below 300°C, nearly the same temperature range of the ΔAbs suppression,

shown in figure 4. The striking correlation between them demonstrates that the formation of the color centers prevents the blue emission. Significantly, neither UV-irradiation effect nor the post annealing one is detected in the conventional Ti-Al₂O₃ prepared in reduced atmosphere. This fact implies that in oxidized Ti-Al₂O₃ the excess oxygen ions, which are necessary to generate tetravalent Ti⁴⁺, or structural distortion due to the excess oxygen act as trapping centers for photo-excited carriers.

As can be seen in figure 5, the increase of the blue emission overshoots the intensity of the as-grown crystals (broken line), whereas the intensity of the ceramics samples reaches to the initial value (solid line). Similar overshooting is found in the absorption spectrum of the single-crystal: ΔAbs is suppressed below the initial value (broken line) as shown in figure 4. Actually, a weak bump is seen at about 400 nm in the absorption spectrum (figure 1) of the as-grown single-crystal. These results suggest the color centers existing in the as-grown single-crystals. Such the color centers are probably introduced by the UV-irradiation during the crystal growth process. This is because a Xe-discharge lamp, which is employed as a light source of the present floating-zone furnace, emits rather intense UV light.

4. Summary

Optical properties have been investigated in both single-crystalline and ceramics samples of oxidized Ti-Al₂O₃. The charge-transfer transitions from 2p states of O²⁻ to 3d ones of Ti⁴⁺ are observed as the absorption band below the fundamental absorption edge of Al₂O₃. The photo-excitation for this band gives rise to the intense blue photoluminescence. The photo-excited electrons are in part trapped, leading to the color centers observed as the absorption peak below the charge-transfer band. As the result, the blue emission is greatly suppressed in the UV-irradiated samples. The trapped electrons are restored to the ground state by the post-annealing.

Acknowledgments

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