PHYSICAL REVIEW B VOLUME 19, NUMBER 6 15 MARCH 1979

Luminescence of the *F* center in sapphire

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(Received 25 September 1978)

An *F*-center emission band (3 eV) has been observed in subtractively colored Al_2O_3 crystals upon exciting with *F* light (6.1 eV). The lifetime of the 3 eV luminescence is 36 ± 4 msec. We attribute this long lifetime to the forbidden triplet-to-singlet transition of the *F* center. The $F \leftrightarrow F^+$ conversion can be shown by studying the *F* and F^+ emission bands in these crystals.

I. INTRODUCTION

On the basis of an extensive study[1] of the optical behavior of neutron-bombarded crystalline sapphire we proposed that oxygen vacancies with one electron (F^+ centers) and two electrons (*F* centers) are responsible for the 4.8 and 6.1 eV absorption bands, respectively. This defect model has been supported by the recent experimental studies of Evans,[2,3] who, in addition, found evidence for attributing absorption at 5.4 and 6.0 eV to the F^+ center as well.

Our recent studies in this area have concentrated on the luminescent behavior of both *F* centers and F^+ centers. Although F^+-center luminescence at 3.8 eV has become well known, *F*-center luminescence has hitherto not been identified. In this work we have used crystals colored by fast neutrons, but we have especially used "subtractively colored" crystals prepared by heating in a graphite crucible under strongly reducing conditions at 2000 °C.[4] The term "subtractive coloration" is used because the color centers result from the extraction of oxygen atoms, through the decomposition vapor pressure of Al_2O_3 at this very high temperature, rather than the introduction of aluminum atoms from a vapor phase rich in aluminum (additive coloration). Basically, the thermochemical process is the same for both coloration methods. The advantage of thermochemically colored crystals for these studies is that the concentration of deep electron traps is small enough that *F*-center luminescence is visible.[5] Also, except for electron excess color centers (*F*, F^+, and possible *F*-type cluster centers), no other complicating defect centers, e.g., interstitial oxygen clusters, are present.[6] Impurity traps play a role in these studies, and their influence varies with crystal purity from one sample to another. The annealing of subtractively colored samples also contrasts strongly with crystals colored by bombardment. The *F* centers in the latter start disappearing at temperatures as low as 300 °C and are completely gone by 900 °C. Annihilation presumably takes place between these vacancy centers and oxygen released from interstitial oxygen clusters. The thermochemically introduced *F* centers are stable up to 1400 °C and annealing in air (oxygen) is necessary for their destruction.[7] Therefore, some type of inward diffusion process involving the oxygen appears to be necessary.

In addition to deliberately colored crystals, there have been reports of a 6.1 eV absorption band, a 6.05 eV photoconductivity band, and 3 and 3.8 eV luminescent bands in certain "as-grown" crystals.[8,9] In this paper we will show that these optical bands are associated with *F* and F^+ centers that result from crystal growth under sufficiently reducing conditions. Therefore, control of the ambient during crystal growth is an important criterion for uv quality sapphire crystals.

II. EXPERIMENTAL PROCEDURE

Sapphire crystals were obtained from three sources: Material Research Co., Union Carbide Co., and Adolf Meller Co. The procedures for subtractive coloration have been described in a previous publication. Neutron bombardment was performed in the North Carolina State University Pulstar reactor which has a flux of 10^{13} reactor spectrum neutrons/cm^2 sec. The emission detection system consisted of an RCA C-31034 photomultiplier tube mounted on a 0.5-m Jarrell-Ash monochromator with a dispersion of 16 Å/mm. A Keithley 610C electrometer is used to amplify the signal. Excitation spectra were taken using light from either a 150-W xenon short-arc discharge lamp or a 45-W deuterium lamp which was dispersed by a Bausch and Lomb high-intensity monochromator. Photoconductivity was measured on samples mounted in a liquid-nitrogen cryostat fitted with a fused silica window. The platinum electrodes were sputtered onto opposite surfaces of Al_2O_3 samples. Photocurrents were detected with a Cary Model 401 vibrating reed

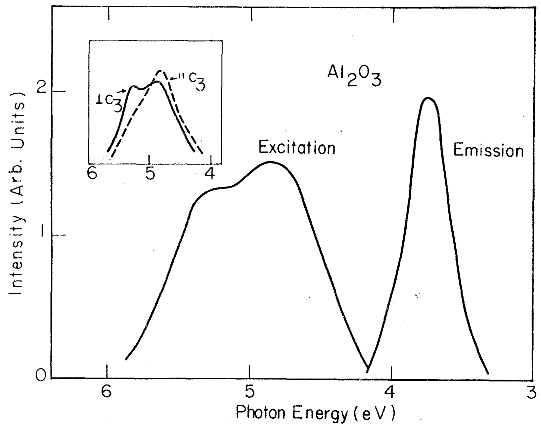

FIG. 1. Excitation and emission spectra of the F^+ center from subtractively colored Al_2O_3 measured at 300 K.

electrometer. Fluorescence lifetime measurements were made with a Xenon Corp. fast extinguishing flash tube FP-10A, a Tektronix 7514 storage oscilloscope, and an associated emission detection system.[10] The resolution of the lifetime-measurement apparatus was about 1 μsec. The 77-K measurement was made by immersing the sample into liquid nitrogen in a quartz ESR dewar.

III. RESULTS AND DISCUSSIONS

The excitation and emission spectra of the F^+ center of a subtractively colored Al_2O_3 are shown in Fig. 1. The 3.8 eV emission band is observed upon exciting with 4.8 or 5.4 eV light. The same spectra can be observed in Al_2O_3 crystals bombarded with high-energy particles.[1,3] The inset of the Fig. 1 shows the polarization of the 4.8 and 5.4 eV bands for the polarizer oriented along the C_3 axis of crystal, $\vec{E} \parallel \vec{C}_3$, or perpendicular to the C_3 axis, $\vec{E} \perp \vec{C}_3$. From the inset it is clear that 5.4 eV band is strongly polarized. The polarization behavior of the 5.4 eV band has been noted previously by Evans.[2] The F^+ center in Al_2O_3 has C_2 symmetry, which cause the $2p$ state to split into $1B$, $2A$, and $2B$ states. Evans[2] assigned the $1A \rightarrow 1B$, $1A \rightarrow 2A$, and $1A \rightarrow 2B$ transitions to the 4.8, 5.4, and 6.0 eV absorption bands, respectively. For electric-dipole transitions in C_2 symmetry centers, only σ transitions are allowed for $A \rightarrow A$ and only π transitions are allowed for $A \rightarrow B$. The Z axis of the F^+ center is parallel to the C_2 axis which is perpendicular to the C_3 axis. Therefore, the σ transition should exhibit very strong preference for the case $\vec{E} \perp \vec{C}_3$, and this is consistent with the assignment of the 5.4 eV band to the $1A \rightarrow 2A$ transition. The F^+ center in Al_2O_3 can occupy three equivalent sites and the Z axis (C_2 axis) of each site differs by 120° from the other Z axes. Previously, we assumed that the electric dipoles of the 4.8 eV band could be described by a linear combination of π_x and π_y, $K(\pi_x + \pi_y)$ and calculated that the intensity for $\vec{E} \parallel \vec{C}_3$ was slightly larger than for $\vec{E} \perp \vec{C}_3$.[1] This result agrees with the assignment of the 4.8 eV band to the $1A \rightarrow 1B$ transition.

In addition to the 3.8 eV band as shown in Fig. 2, we observe a 3.0 eV emission band in a sub-

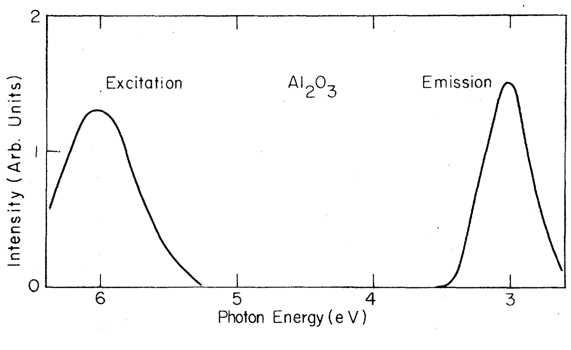

FIG. 2. Excitation and emission spectra of the F center from subtractively colored Al_2O_3 measured at 300 K.

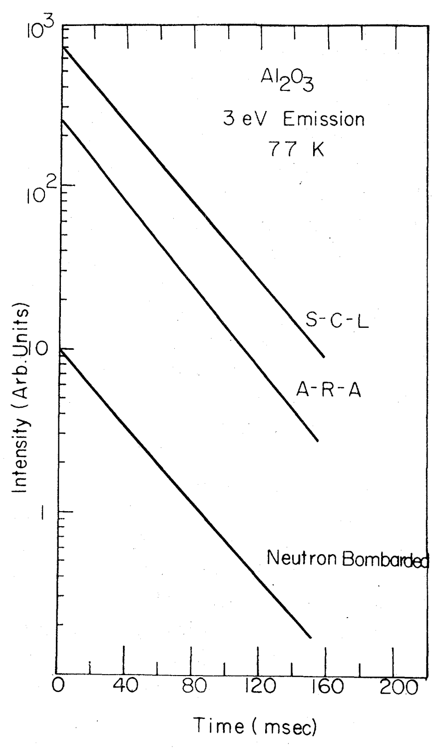

FIG. 3. Semilogarithmic plots of the decay of the 3 eV emission at 77 K from subtractively colored Linde (SCL), neutron-bombarded, and as-received Adolf-Meller ARA samples.

tractively colored Linde sample (SCL sample) and an as-received Adolf-Meller sample (ARA sample). The high-energy particle-bombarded samples do not exhibit a readily apparent 3.0 eV emission band. However, our lifetime measurement does show that the same 3.0 eV emission band can be detected in a bombarded sample (Fig. 3). As shown in Fig. 2, the 6.1 eV band is the only excitation band in the spectral range from 3.5 to 6.4 eV. The 3 eV stokes shift between the excitation and the emission is quite large. In Fig. 3 there is shown a semilogarithmic plot of the decay of the 3 eV emission at 77 K from a SCL, a neutron-bombarded, and an ARA sample. The slopes of the curves indicate that the lifetime of the emission is 36 ± 4 msec for the three differently treated samples. A large Stokes shift and a long lifetime suggest that the emission (3 eV) is associated with a forbidden transition of the *F* center. The electronic structure of the *F* center can be treated as a helium atom. The ground-state configuration $(1s)^2$ corresponds to the term $^1S_0$. Excited states of the helium like system are generated by promoting one electron into a $2s$ or a $2p$ state, the excited-state configuration then being $1s2s$ or $1s2p$, there being singlet and triplet states (^1S, ^3S, ^1P, and ^3P) for both of these excited configurations. Emission from *F* centers[5,11] in both CaO and MgO is observed by pumping into the $^1S \rightarrow {}^1P$ absorption band. The emission corresponds to the transition $^3P \rightarrow {}^1S$ of the *F* center, the ^3P state being occupied by radiationless decay from the higher ^1P state. Thus the Stokes shift between excitation and emission energies is large and the lifetime for the $^3P \rightarrow {}^1S$ emission is long for the *F* center in both MgO and CaO.[11] By analogy with these cubic oxides, it is expected that the 6.1 eV absorption band and 3 eV emission band originate from $^1S \rightarrow {}^1P$ and $^3P \rightarrow {}^1S$ transitions of the *F* center, respectively, in Al_2O_3.

Lehmann and Gunthard[8] reported that the decay of 3 eV emission intensity involves a first-order process component with a temperature-independent lifetime of 36 ± 4 msec and is followed by a strong temperature-dependent second-order process component. The second-order process component lasts for about 5 sec at 300 K. Lehmann and Gunthard calculated[8] the kinetics of 3 eV emission from a model which consists of an inpurity and a metastable state. The results agree with the experimental data. As mentioned above we attribute the long 36 msec, temperature-independent component (Fig. 3) to the forbidden triplet-to-singlet transition of the *F* center. We found that the temperature dependence was sensitive to specimen origin. At 300 K, the ARA sample shows only the 36 msec component, but the SCL sample shows both components (Fig. 4). Impurity release of electrons from impurity traps has been suggested as the origin of the phosphorescent component of the *F* center in CaO.[11] We believe that the same situation applies in Al_2O_3. The impurity trapping model involves the capture and subsequent release of one of the *F*-center electrons which is freed upon *F*-center excitation. Photoconductivity measurements indicate that charge carriers are created by illuminating with *F*-center light (Fig. 5). The 6.1 eV photoconductivity band has been reported by previous investigators.[9,12] Summers[13] observed that the intensity of 6.1 eV photoresponse band at 10 K is about the same as at 300 K, which

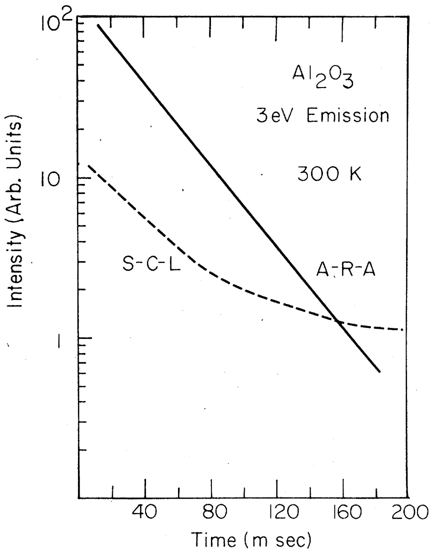

FIG. 4. Semilogarithmic plots of the decay of the 3 eV emission at 300 K from SCL and ARA samples.

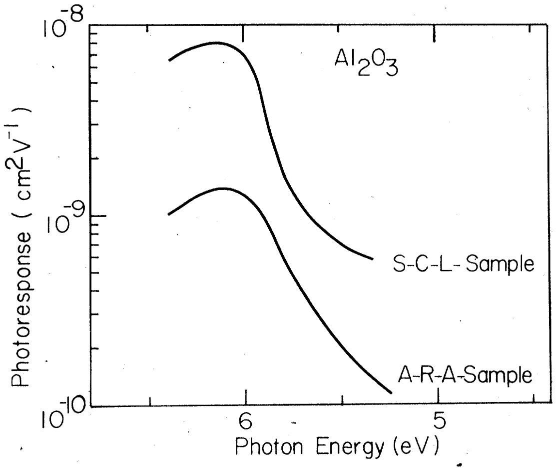

FIG. 5. Spectral dependence of the photoresponse at 300 K from SCL and ARA samples.

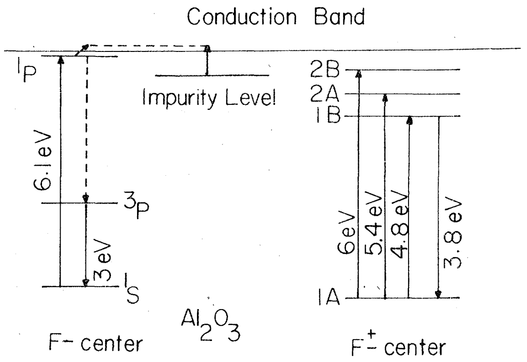

FIG. 6. Energy-level scheme for absorption and emission processes associated with F and F^+ centers in Al_2O_3.

indicates that the 6.1 eV band is very close to conduction band. The evidence of carrier release from impurity traps comes from the fact that the SCL sample shows a 3.0 eV thermoluminescence (TL) peak near room temperature after 6.1 eV light irradiation at 77 K but the ARA sample does not. In fact, we can detect no TL in the ARA sample which has been previously exposed to 6.1 eV light at 77 K and then warmed up to 500 K. Figure 6 shows the energy-level scheme for absorption and emission processes associated with F and F^+ centers in Al_2O_3.

In a previous study of neutron-bombarded samples,[1] we observed the reciprocal relation between the 4.8 and 6.1 eV bands. Irradiation into the 6.1 eV band enhances the 4.8 and 5.4 eV bands. In these heat-treated samples, the intensity of 6.1 eV absorption band is not appreciably affected by the uv-light bleaching, which makes it difficult to observe the $F \rightarrow F^+$ conversion from absorption spectral measurements. However, as shown in Fig. 7, the intensity of the F^+ emission band (3.8 eV) increases substantially upon bleaching with 6.1 eV light and this is clear evidence that the F centers convert to F^+ centers. It is also apparent from Fig. 7 that the intensity of 3.8 eV band decreases by about a factor of 10 if the sample is annealed at 1200 °C in air for 10 min. That high-temperature annealing converts the F^+ centers to F centers has also been observed in additively colored MgO samples.[5] A more direct observation of $F \rightarrow F^+$ conversion in this heat-treated sample comes from a study of the intensity of the F^+ luminescence (3.8 eV) with or without the F-center light (6.1 eV) irradiation. Figure 8(a) shows that the F-center luminescence (3.0 eV) increases in intensity during the first few seconds and then reaches saturation after about 5 sec of F light (6.1 eV) excitation. In the first few seconds of irradiation the F electrons released by F-light absorption are captured by both empty traps and F^+ centers. As soon as the traps are filled, all of the ionized electrons will be captured by F^+ centers and contribute to the 3.0 eV luminescence. Thus the luminescent intensity first increases and then saturates.

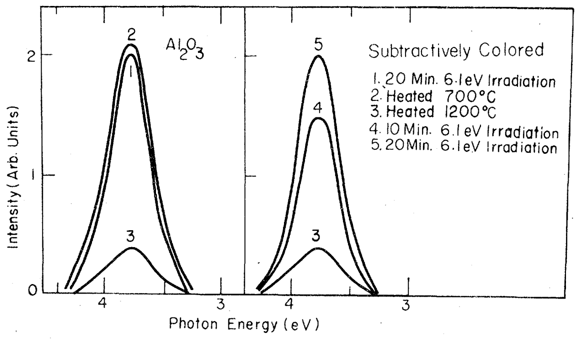

FIG. 7. Variation of 3.8 eV emission at 300 K in a subtractively colored Al_2O_3 with sample treatment (1) after 20-min 6.1 eV light irradiation; (2) after heating at 700 °C in air for 10 min; (3) after heating at 1200 °C in air for 10 min; (4) after 10-min 6.1 eV light irradiation; (5) after 20-min 6.1 eV light irradiation.

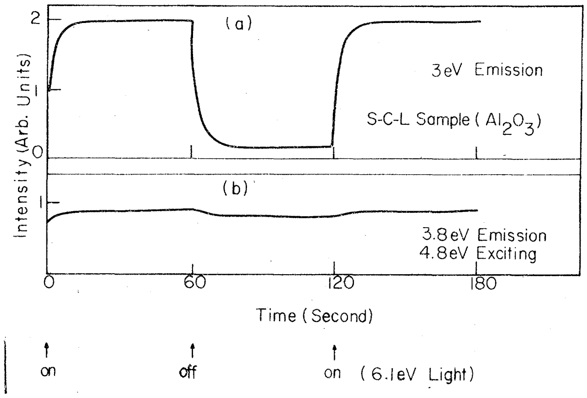

FIG. 8. Effect of 6.1 eV light irradiation on (a) 3 eV emission, (b) 3.8 eV emission in a SCL sample measured at 300 K.

We also monitored the 3.8-eV F^+-center luminescence by exciting into the 4.8-eV F^+ band during the 6.1 eV excitation cycle [Fig. 8(b)]. By keeping the 4.8 eV light constant while the 6.1 eV light was turned on and off a time record of the F^+-center concentration was obtained. As would be expected, the F^+ luminescence increases during the first few seconds of 6.1 eV excitation and saturates as does the F luminescence, indicating once again that in the initial period of excitation F-center electrons are transferred to traps, thus enhancing the F^+-center concentration. When the 6.1 eV exciting light is turned off, the intensity of the 3.8-eV F^+ emission decays with about the same period of the F-center phosphorescence to its original value, which indicates that electrons released from traps recombine with F^+ centers to restore the F-center density. To exclude the possibility that the change in 3.8 eV light intensity might be due to the tail of the 3.0-eV F-center luminescence rather than to the F^+ center, we monitored this emission wavelength when only 6.1 eV exciting light was used. A very small abrupt change was observed upon turning the 6.1 eV excitation on and off. Therefore, we conclude that the 3.8 eV emission originates with F^+ centers created by F-center ionization.

ACKNOWLEDGMENT

The authors are grateful to G. P. Summers for furnishing us with an Adolf-Meller crystal, to J. K. Nagle for helping with lifetime measurements, and to D. J. Eisenberg for helping with photoconductivity measurements. Thanks are also due to W. L. Dunn of the Nuclear Engineering Department of NCSU for providing neutron irradiations. We are also grateful to the UNC-CH University Research Council for providing certain items of equipment used in this research. The work was supported by the Department of Energy under Contract E-40-1-3677.

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