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EFFECT OF IONIZING RADIATION ON RUBY

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Lewis Research Center

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SUMMARY

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The ability of ruby to operate as a laser is dependent on the presence of chromium^{+3} (Cr^{+3}) impurity ions. Since radiation can cause severe ionization effects in ionic solids, it is desirable to determine whether ruby would be affected by such a radiation field. High-purity ruby and α-aluminum oxide (α-Al_2O_3) were studied by optical absorption and electron paramagnetic resonance techniques both before and after irradiation with high-energy X-rays. Irradiation of ruby crystals which have been preannealed in air results in a 20-percent loss of Cr^{+3}, the formation of Cr^{+4} and Cr^{+6} ions, and an unidentified V-type defect center. The effects found indicate complex interactions which depend strongly on the crystal pretreatment, purity, and irradiation dose. Probable ionization processes are given to account for the results observed.

Author

INTRODUCTION

The operating principle of the ruby laser depends on the optical excitation of the chromium^{+3} (Cr^{+3}) electron and the subsequent fluorescence accompanying the stimulated transition of this electron from a metastable excited state to the ground state. It follows, then, that any process which significantly alters the concentration of Cr^{+3}, or the population of electron states of the Cr^{+3} ion, will affect laser operation.

Both particle radiation and electromagnetic radiation have been shown to interact with atoms in ionic solids so as to cause excitation and ionization of a somewhat permanent nature. For higher energy radiations, displacement of the atoms can occur to produce large concentrations of crystal lattice vacancies, interstitials, and other more complex defects. These displacement defects can also affect the electron state populations by trapping electrons or holes excited from impurity ions by the irradiation.

From a practical viewpoint, the radiation effects from high-energy X-rays, γ-rays, and neutrons are of more interest because of their greater penetrating ability. Charged particle radiations, having shorter ranges, may usually be effectively shielded out.

Moreover, from a more fundamental viewpoint, the study of high-energy X-ray, or γ-ray irradiation of ruby has several distinct advantages: (1) ionization effects predominate and thus permit study of these processes independent of complicating displacement effects; (2) impurities and/or residual radioactivity is not introduced into the crystal; and (3) some background has been acquired from other X-ray or γ-ray studies as to the type of behavior to be expected.

Several authors have investigated the effect of ionizing radiation on "pure" α-aluminum oxide (α-Al_2O_3) (refs. 1 to 8). Most of these authors report saturation of optical absorption changes at relatively low X- or γ-radiation exposures, which indicates the involvement of an entity in low concentration. Less agreement was apparent as to the nature of the absorption spectra obtained. Only a few of these authors attempted to associate the observed bands with particular electron transitions. Where this was attempted, the bands were believed to be associated with displacement defects rather than impurities in the Al_2O_3 lattice. The lack of general agreement, however, suggests that more is involved here than simple defect production; it appears that the presence of some impurity may be involved.

In contrast to pure Al_2O_3, little work has been done on ruby itself (refs. 8 and 9). The work of references 8 and 9 was somewhat preliminary, and again, no definite assignments of the optical absorption bands were made.

This report extends knowledge of the effect of ionizing radiation on ruby as it relates to its use as a laser. Specifically, the extent and manner in which the radiation interacted with the samples were determined by optical absorption and electron paramagnetic resonance (EPR) techniques. Based on the spectra obtained, assignment of individual bands to specific electronic transitions is suggested.

EXPERIMENTAL APPARATUS AND PROCEDURE

The ruby and Al_2O_3 samples used were commercially prepared. The ruby samples were disks 1/16-inch thick and 3/8-inch in diameter, oriented with the c-axis 60° from the disk axis and made from laser quality material with 0.05 percent Cr^{+3}. The Al_2O_3 samples were the same size and had the same orientation as the ruby and were specially selected for high purity.

The samples were polished, notched for alinement purposes, and then annealed in air for 1 hour at 1000° C before any experiments were carried out. All optical absorption data were obtained at room temperature by using a double-beam recording spectrophotometer. The absorption spectrum from 6.5 to 1.65 electron volts (1900 to 7500 Å) was recorded for all samples.

One of the ruby samples was cut into slivers approximately 1/16 by 1/16 by 3/8 inch

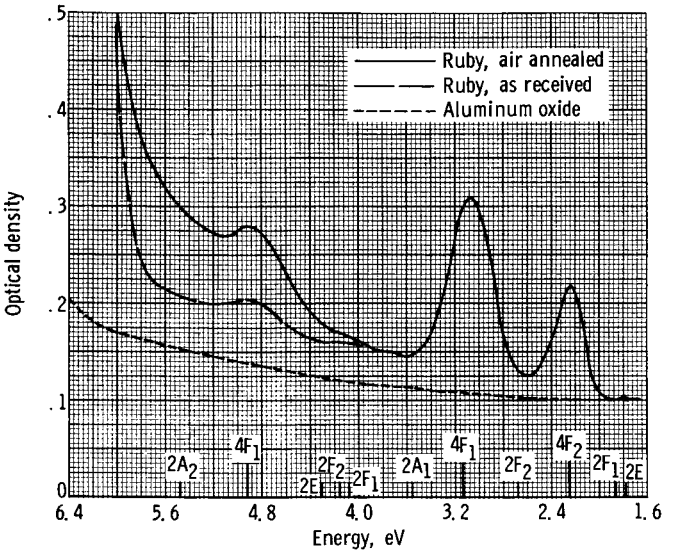

Figure 1. - Absorption spectra of unirradiated ruby and aluminum oxide. Spectra include apparent absorption due to surface reflection.

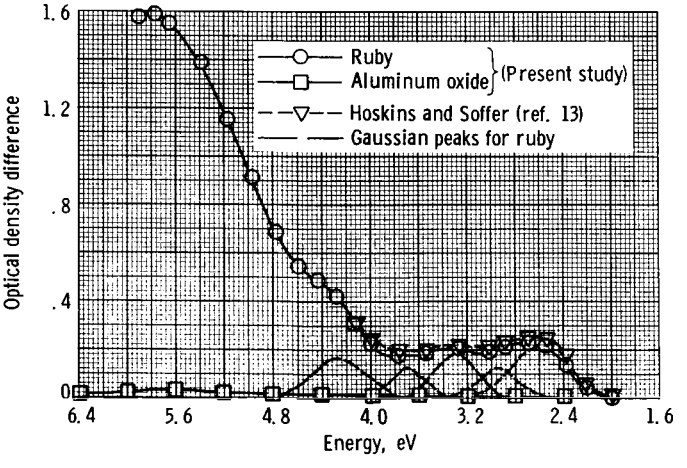

Figure 2. - Typical X-ray-induced absorption spectra of ruby and aluminum oxide. Spectrum for ruby is resolved into component bands.

These slivers were used for EPR studies in a conventional EPR spectrometer operated at a cavity resonance frequency of 9.1 gigahertz (X-band). Measurements were taken at room temperature, liquid-nitrogen temperature, and liquid-helium temperature.

Irradiation of the samples was carried out by using an industrial X-ray unit operated at 300 kilovolts and 8 milliamperes. The X-ray tube had a copper target and was equipped with a beryllium window. The samples were exposed, at a constant dose rate, while on a rotating table about 9 inches from the copper target. All irradiations were done in air at room temperature. A calibrated polystyrene ionization chamber with a volume of 0.028 cubic centimeter replaced the samples in the measurement of the X-ray dose. The dose reported is the measured dose and not the ionization in the samples.

RESULTS

The ultraviolet and visible absorption spectra of pure Al_2O_3 were obtained before and after irradiation to determine any changes due to the host lattice. The results are shown in figure 1 and 2. In contrast to the results reported in several literature references, no absorption bands were found either before or after the irradiation. This apparent disparity between the present results and others is thought to be related to the very high purity of the present samples. This point is discussed again on pages 6 and 7.

Figure 1 also includes the absorption spectrum for unirradiated ruby. Above 4 electron volts some difference was found between as-received crystals and those annealed in air. (The as-received ruby crystals gave a spectrum in very good agreement with that of Maiman, et al. (ref. 10).) The present data are consistent with the spectrum

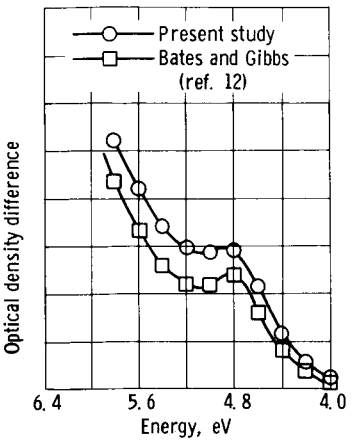

Figure 3. - Optical density difference between as-received and air annealed ruby below 5.8 electron volts.

calculated by Tanabe and Sugano (ref. 11) for Cr^{+3} if the absorptions are assumed to arise from transitions from the $4A_2$ ground state. The energies of these bands are marked along the abscissa of figure 1. The more probable transitions are those to the $4F_1$ and $4F_2$ states. The crystal field parameters, D_q, which equals 1860 centimeters^{-1}, and B, which equals 693 centimeters^{-1} used in this report to calculate these energies are reasonable for Cr^{+3} in Al_2O_3. An absorption edge for ruby is indicated at about 6.2 electron volts. The band gap for Al_2O_3 is 8.8 electron volts.

It is interesting to compare the spectrum of the as-received and the air annealed ruby in figure 1. The difference curve for these two spectra in the region above 4 electron volts is shown in figure 3. Also plotted is the "excess oxygen" spectrum of Bates and Gibbs (ref. 12) obtained from Al_2O_3 preheated in air above 1300° C. Because a different annealing temperature was used in the present work, an arbitrary density scale was used in this comparison. The conditions for occurrence of these bands in preannealed ruby and Al_2O_3 is discussed on page 6.

After irradiation of the annealed ruby with X-rays, profound changes were observed in the optical absorption spectra. Figure 2 shows the spectrum due to the irradiation; the spectrum for unirradiated ruby has been subtracted out. Four pronounced bands can be resolved at 2.6, 3.3, 4.3, and 5.8 electron volts. (Because of the strong absorption near the edge at 6.2 eV, reliable density subtraction can be made only up to about 5.9 eV.) If a Gaussian shape is assumed for the bands, two additional bands at approximately 3.0 and 3.7 electron volts can be obtained from the residuals, but with less certainty. Below 4.2 electron volts the spectrum compared almost exactly with the absorption data of Hoskins and Soffer (ref. 13), who grew chromium-doped Al_2O_3 crystals under conditions which favored the formation of Cr^{+4} ions. However, these authors do not ascribe the observed bands to Cr^{+4}, but rather to a doubly charged anisotropic center probably associated with anionic charge compensation in their crystals.

Above 5 electron volts the very strong absorption observed indicates either an entity in higher concentration than the Cr^{+3} ion or a center of very high oscillator strength. The spectrum does not coincide with the "excess oxygen" bands observed before irradiation, and its high density does not permit a comment on the presence of the "excess oxygen" bands after irradiation.

The entire spectrum of the X-irradiated ruby was saturated at about 5×10^5 roentgens This is shown in figure 4 for the band at 5.8 electron volts; however, essentially identical curves were obtained for the other bands. The uniformity of saturation and also of

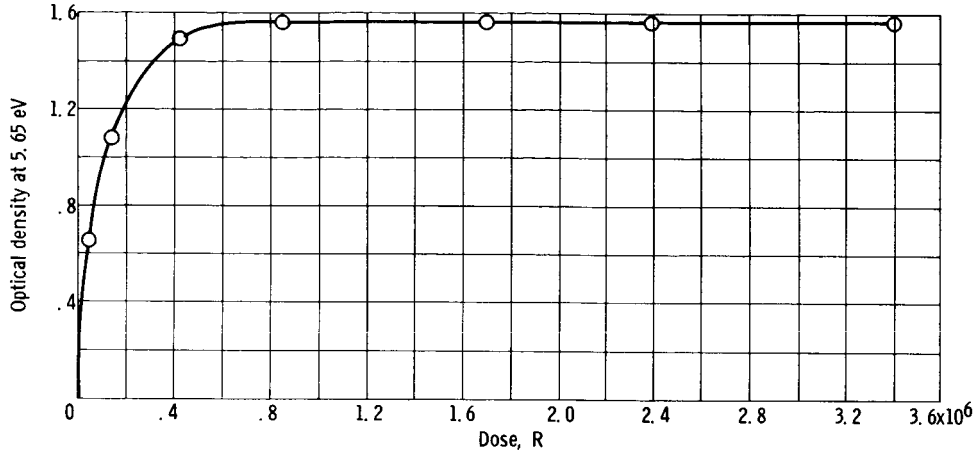

Figure 4. - Saturation of induced absorption for 5.8-electron-volt band shown in figure 2. Value at 5.65 electron volts was plotted instead of peak value at 5.8 electron volts because peak was not well defined at low dose.

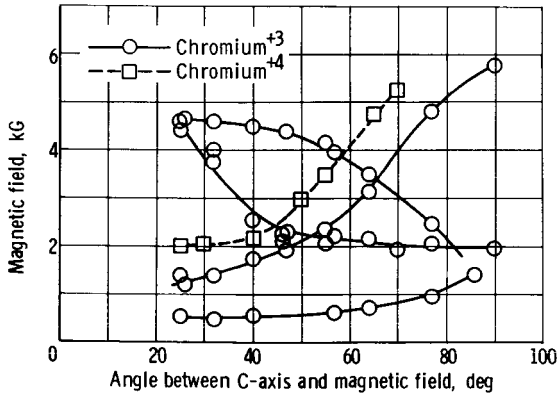

Figure 5. - Angular variation of fine structure lines of chromium^{+3} in irradiated ruby sample taken at room temperature and 9.1 gigahertz. (C-axis was inclined about 23° to plane of magnetic field.)

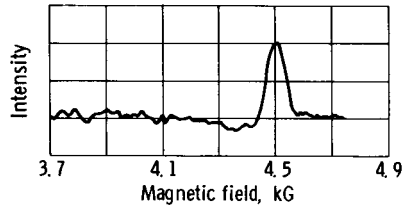

Figure 6. - Observed asymmetric line shape of line producing dashed curve of figure 5.

annealing behavior suggests a single process or transition (or two or more interrelated processes) giving rise to the observed spectrum.

EPR studies of the irradiated ruby at 4° K in the spectral region from 0 to 10 kilogauss indicated the presence of several faint lines in addition to those due to the Cr^{+3} ion. The position of one of these faint lines in relation to the known Cr^{+3} spectrum for various crystal orientations is shown as the dashed curve of figure 5. The solid curves shown are a best fit drawn through the observed Cr^{+3} line positions and represent an extension of the known Cr^{+3} spectra (ref. 7) to lower fields. The dashed curve was an extremely good fit to the single line which Hoskins and Soffer (ref. 13) attributed to Cr^{+4} in their Cr^{+4} doped Al_2O_3. The observed asymmetric line shape and line width (fig. 6) also coincide with that for the Cr^{+4} line of Hoskins and Soffer. The intensities of the Cr^{+3} lines were decreased after irradiation and indicated reductions of as much as

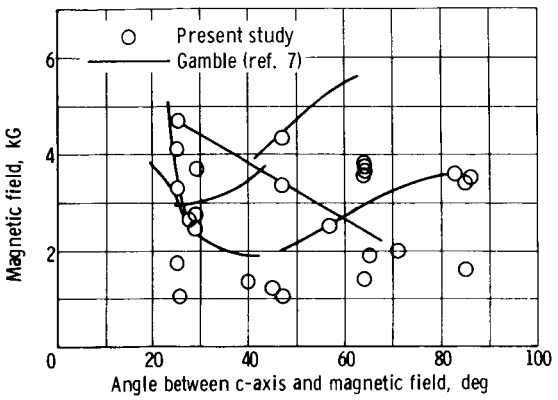

Figure 7. - Electron paramagnetic resonance spectrum of iron^{+3} obtained by Gamble (ref. 7) and data from present study.

20 percent in the concentration of the Cr^{+3} ion.

The other faint lines found are shown separately in figure 7 as the data points. The solid curves here are the iron^{+3} (Fe^{+3}) spectra obtained by Gamble (ref. 7). It is evident that, except for several lines found in the present irradiated ruby spectra at about 3.6 kilogauss, most of the other weak lines fit the Fe^{+3} spectrum. The lines found below 2.0 kilogauss, for which no comparison is possible, may also be due to Fe^{+3}. The presence of these weak iron lines found in the spectra for irradiated ruby and some weak iron lines found in unirradiated ruby is consistent with a spectrographic analysis which indicated iron in trace amounts.

DISCUSSION

Preannealing ruby in air significantly influences the effects produced by ionizing radiation. It is generally believed that the additional oxygen from the air which is adsorbed on the crystal can oxidize certain of the cation impurities (e.g., Cr) and in so doing become oxygen ions. The lattice containing these additional ions is cation deficient at the surface, and the cation vacancies migrate throughout the crystal at the annealing temperature.

Bates and Gibbs (ref. 12) suggest a similar mechanism for their Al_2O_3 heated in air, and Peria (ref. 14) remarks on an analogous situation with iron doped magnesium oxide. The absorption bands obtained by the latter author are similar in character to the "excess oxygen" bands and correlated strongly with the Fe^{+2} concentration present. Peria suggests that these bands arise coincidently with the formation of Fe^{+3} ions, but that it should not be concluded that they are due to Fe^{+3} transitions rather than to a defect center simultaneously produced.

The fact that the present annealed, high-purity Al_2O_3 crystals did not show the "excess oxygen" bands indicates that the presence of a charge compensating impurity ion is required. Unknown and variable impurity content may account for the differences found in the optical absorption spectra of irradiated Al_2O_3 by several authors mentioned previously.

In the annealed ruby the Cr^{+3} ion would be expected to act as the charge compensator by one of the following processes:

$$Cr^{+3} + O^0 \rightarrow Cr^{+4} + O^{-2}$$

$$Cr^{+3} + O^0 \rightarrow Cr^{+5} + O^{-2}$$

$$Cr^{+3} + O^0 \rightarrow Cr^{+6} + O^{-2}$$

While the Fe^{+3} impurity may also be oxidized, it is less likely to be oxidized than Cr^{+3}. Thus, prior to irradiation, the annealed ruby crystal contains Cr^{+3}, chromium in a higher oxidation state, cation vacancies, and trace impurities such as Fe^{+3}.

As was mentioned previously, the predominant effect of irradiation with X-rays would be ionization. After irradiation a 20-percent reduction in Cr^{+3} was observed, as well as the presence of some Cr^{+4}, some Fe^{+3}, and a weak center. This center gives rise to an EPR line at 3.6 kilogauss. Also noted were an intense ultraviolet absorption at 5.8 electron volts and other less intense bands at lower energies which correspond to an undetermined defect center. The following mechanisms are supported by these findings, coupled with other literature work.

The intense absorption at 5.8 electron volts arises from charge transfer transitions due to Cr^{+6} (CrO_4^{-2}). The very high oscillator strength, energy, and band width of these bands substantiate this assignment. The appearance of the Cr^{+6} band and the Cr^{+4} EPR spectrum only after irradiation suggests that the Cr^{+3} is oxidized only to Cr^{+5} (CrO_4^{-3}) in the annealing. Charge transfer bands for this ion have been postulated (ref. 15), but their energy spectrum in this host lattice is unknown. During the irradiation a Cr^{+5} electron may be promoted to the conduction band, be trapped elsewhere, and leave Cr^{+6}, or an additional electron may be trapped by Cr^{+5} to form Cr^{+4}. Some Cr^{+4} may also be produced by the irradiation induced reaction Cr^{+3} + X-ray $\rightarrow$ $Cr^{+4} + e^-$, which also results in the loss of Cr^{+3}. However, the low intensity of the EPR line due to Cr^{+4} makes it doubtful whether this process causes the 20-percent reduction in Cr^{+3}. Besides, it is likely that Cr^{+5} would act as an electron trap.

The 20-percent loss of Cr^{+3} can be explained by an electron trapping process resulting in the formation of Cr^{+2} ions. Unfortunately, this conclusion has not been directly confirmed, since the Cr^{+2} ion cannot be detected directly by either the present optical absorption or EPR techniques. However, experimental results indicate the formation of Cr^{+2} by irradiation in other oxide crystals (ref. 16), and this process is especially likely to occur in the vicinity of a cation vacancy, which can effectively trap holes (V centers). The V center can be detected by EPR techniques as a single line spectrum located at about 3.6 kilogauss at X-band frequencies (ref. 17).

CONCLUDING REMARKS

The effect of even low-energy electromagnetic radiation can cause marked changes in the ionization state of chromium in ruby which could significantly affect its operation in a laser device. The changes to be expected are complex and depend strongly on the crystal pretreatment and purity and on the presence of crystal defects.

Lewis Research Center,
National Aeronautics and Space Administration,
Cleveland, Ohio, February 2, 1966.

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