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Study of Ionization-Induced Radiation Damage in MgO†

Y. Chen and W. A. Sibley
Solid State Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee

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A study of the 2.3-eV absorption band in MgO crystals irradiated with electrons and gamma rays at 7, 80, and 305°K has been made. This broad band, which has been designated as V_1, has a half-width of 0.96 eV at 5 and 78°K and could be optically bleached even at liquid-helium temperature. When specimens were bleached with polarized light, it was found that there was no dichroism in any of the ⟨100⟩, ⟨110⟩, or ⟨111⟩ directions at 5°K. The colorability of the crystals was strongly dependent on their thermal treatment. The concentration of centers responsible for the 2.3-eV absorption could be enhanced by quenching the crystals from high temperature prior to irradiation and could be suppressed by slow cooling of the specimens to room temperature. The effects of these heat treatments were found to be reversible. The presence of certain impurities in the crystals was observed to suppress the 2.3-eV coloration, but no correlation between the Fe^{3+} concentration or the total Fe concentration and the maximum coloration in a quenched crystal was observed. The afterglow luminescence was also surveyed in the energy range 1.3–5.0 eV.

INTRODUCTION

Even though a considerable volume of information has been accumulated on the ESR properties of impurities and radiation defects in MgO crystals, there has been relatively little research done in the areas of optical absorption and luminescence. Only recently has it been possible to assign absorption bands to two of the more prominent radiation-produced defects, F and V_1 centers, which were identified sometime ago by ESR techniques[1–4]; and furthermore, some defects which should exist in irradiated MgO have not yet been detected. For example, the F' center, which is a negative-ion vacancy with two captured electrons,[5] is stable in the alkali halides at low temperature and because of the divalency of MgO it should be even more stable in crystals of this material. To date, however, this center has not been positively identified.

The lack of optical-absorption data has not only made it difficult to identify specific color centers, but has also hindered progress in the understanding of radiation-defect production mechanisms of MgO. In alkali halides, which are highly ionic, there is now much evidence that radiation defects are produced primarily by ionization events,[5] whereas in semiconductors, which are largely covalent, the production of defects is primarily associated with collision or "knock-on" events.[6] Since the bonding in MgO is not as ionic as the alkali halides and not as covalent as the semiconductors,[7] the question arises as to which defect production mechanism will dominate. This question can be answered by a thorough understanding of the absorption and luminescence properties of irradiated MgO and their dependence on radiation dose. Ionization events normally require a relatively small dose to produce considerable changes in defect structure, whereas the cross section for "knock-on" defect production is much smaller and heavy doses are required to create detectable concentrations of defects.

The work presented here is a general study of ionization-type damage in MgO crystals. Such a study is necessary to determine to what extent ionization participates in the radiation production of imperfections in these crystals. Moreover, there must be an understanding of ionization damage before work can proceed on the effectiveness of "knock-on" processes.

Clarke[8] and Soshea *et al.*[9] have surveyed the effect of ionizing radiation, ultraviolet light and x rays, on the absorption of MgO samples, and found that absorption bands were produced at 5.7, 4.8, 4.3, and 2.3 eV. Soshea *et al.* gave special attention to bands resulting from heat-treatment in oxygen which absorbed light of energy above 4 eV. The absorption and photoconductivity of x-irradiated crystals was also studied by Peria[10]; and he concluded that the bands at 4.3, 4.8, and 5.7 eV were associated with Fe impurity.

The radiation-induced absorption band at 2.3 eV has been ascribed by Wertz *et al.*[4] to positive-ion vacancies which have trapped holes. The positive-ion vacancy with a trapped hole was identified earlier by ESR observations and initially labeled the H_1 center.[11] Later this center was relabeled V_1.[4] Lunsford[12] also investigated the V_1 center using MgO pellets and stated that this center enhanced the catalytic activity for a hydrogen-deuterium exchange reaction. Since Kirklin

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et al.[13] have found that hydrogen can be trapped at V_1 centers, forming what they referred to as the V_{OH} center Lunsford's results are not very unexpected.

Luminescence studies of ultraviolet and x-irradiated MgO have also been made. Many bands have been reported previously,[14–16] but the most reproducible emission bands for relatively pure MgO seem to be around 1.9 and 3.6 eV. Eisenstein[16] has shown that the 3.6-eV band exhibits photoconductivity and decays slowly at room temperature. It can be photostimulated with photon energies of 2.3 and 3.4 eV. He interpreted this in terms of hole release by the photostimulation, an interpretation consistent with one proposed previously by Day.[17] The holes could then annihilate electrons localized on traps at higher energy levels, thus yielding the observed luminescence. This work, together with that of Day, lends further credence to the idea that the absorption band at 2.3 eV is due to a hole center which is probably the V_1.

In our study we investigate the 2.3-eV absorption band and give further evidence that it is associated with the V_1 center. The effect of impurities, heat treatment, and mechanical deformation on the magnitude of this band is studied. We also survey the luminescence properties of crystals obtained from several different sources and the effect of impurities and heat treatment on the luminescence.

EXPERIMENTAL PROCEDURE

In order to study the optical absorption of irradiated MgO crystals cleaved plates of thickness 0.2 cm or less were placed in light-tight sample holders. For room-temperature irradiations, specially built light-tight sample holders were equipped with slides to permit measurement of the absorption spectra of the samples. The irradiations were performed with the holders held in reproducible positions in a 3.0×10^6-R/h Co^{60} gamma source. The irradiation temperature of the samples in the gamma source was controlled to 32±1°C. Irradiations were normally of 20–30-min duration to permit the growth of the absorption band of interest to saturate. For low-temperature irradiations, a Sulfrian liquid-helium cryostat with optical window covers was used in conjunction with a Van de Graaff electron accelerator capable of producing 1.7-MeV electrons at a current density of 0.18 μA/cm^2. The irradiation temperatures ranged from about 7 to 305°K and the optical spectra were normally measured at the irradiation temperature. To obtain the absorption spectra, the holder or the cryostat was placed on slotted adapters in a Cary Model 14R spectrophotometer where the slides or window covers were removed in total darkness.

The luminescence from irradiated MgO was investigated immediately after the radiation was completed and in a few cases during x irradiation. Most of the luminescence measurements were performed at room temperature; however, some data were taken at both liquid-helium and liquid-nitrogen temperatures. The spectral range from 200 to 1100 nm was monitored using three different multiplier phototubes, EMI 9558Q, EMI 6256S, and RCA 7102, in conjunction with a Bausch and Lomb $\frac{1}{2}$m-grating monochromator. The irradiation procedures and precautions were the same as noted above for the absorption experiments.

Only single crystals were used in our investigation and these were obtained from several sources. Table I shows the different samples investigated and gives the concentrations of iron and chromium impurities contained in these crystals. The impurity concentrations were obtained by wet-chemistry, flame-photometry, and nuclear-activation analyses and were found to be reproducible for specimens cleaved from the same crystal to within about 20%.

Iron has always been one or the major contaminants of MgO crystals and is known to be present in three possible valence states, Fe^{+1}, Fe^{+2}, Fe^{+3}.[18] Three of the optical absorption bands in the ultraviolet region have been attributed to Fe,[9,10] and we felt that it would be valuable to investigate this possibility. Figure 1 is a plot of the absorption coefficient of one of these bands

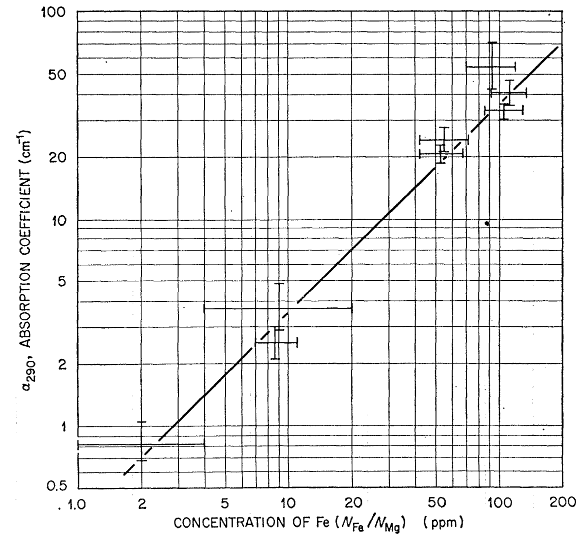

FIG. 1. Absorption coefficient at 290 nm after quenching in argon versus Fe concentration determined from chemical analyses on crystals from General Electric, Harwell, Bristol University, Muscle-Shoals and Norton.

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TABLE I. Crystal designation and impurity concentration of some of the crystals used in this investigation.

Sample	Thickness (cm)	Source	α_{V_1} (cm^{-1})[a]	Estimated[b] V_1 conc. (cm^{-3})	α_{OH} (cm^{-1})	Fe[c] (ppm)	Cr (ppm)
H-36	0.167	Harwell	11	4×10^{17}	0.8	5	<1
H-4	0.145	Harwell	8	3×10^{17}	1.6	80	<1
GE-2,4,5,	0.082 0.167 0.186	General Electric	7	3×10^{17}	1.6	5	<1
MS-12,15 16,19	0.051 0.140 0.122 0.213	Muscle-Shoals	11–17	4–6×10^{17}	0.3	52	20
B-2,3,4	0.149 0.135 0.134	Bristol	10–11	3×10^{17}	0.8	10	2
N-13-Mn	0.121	Norton	0	0	2.9	···	···
MS-2Y	0.121	Muscle-Shoals	14	5×10^{17}	0	100	15

[a] This represents the maximum absorption coefficient that can be introduced in a quenched crystal by radiation.

[b] In order to obtain the V_1 concentrations listed we used a Gaussian form of Smakula's equation (Ref. 5) and chose an oscillator strength of 0.15, half-width of 0.96 eV, and index of refraction of 1.74.

[c] For an independent analysis of the GE samples, see R. L. Hansler and N. G. Segelken, J. Phys. Chem. Solids **13**, 124 (1960) and G. A. Slack, Phys. Rev. **126**, 427 (1962).

(290 nm) versus the Fe concentration determined by chemical analysis for several different samples. The absorption data were obtained after the crystals were irradiated for 30 min in the gamma source. Prior to irradiation each sample was quenched after heating for 5 min in argon at about 1100°C. Irradiation increased the 290-nm absorption to a saturation value. The correlation of the band, obtained in this manner, and the total concentration appears to be fair; however, it should be mentioned that no correlation could be obtained in the case of unirradiated crystals. Thus, an estimate of the total Fe concentration in MgO crystals for concentrations of less than 100 ppm can be obtained by measuring the 290-nm absorption band. The OH^- concentration of the specimens has not been determined quantitatively, but the percent transmission at 3.3 μ which we will take as a measure of the OH^- present[13] is listed for each crystal in Table I.

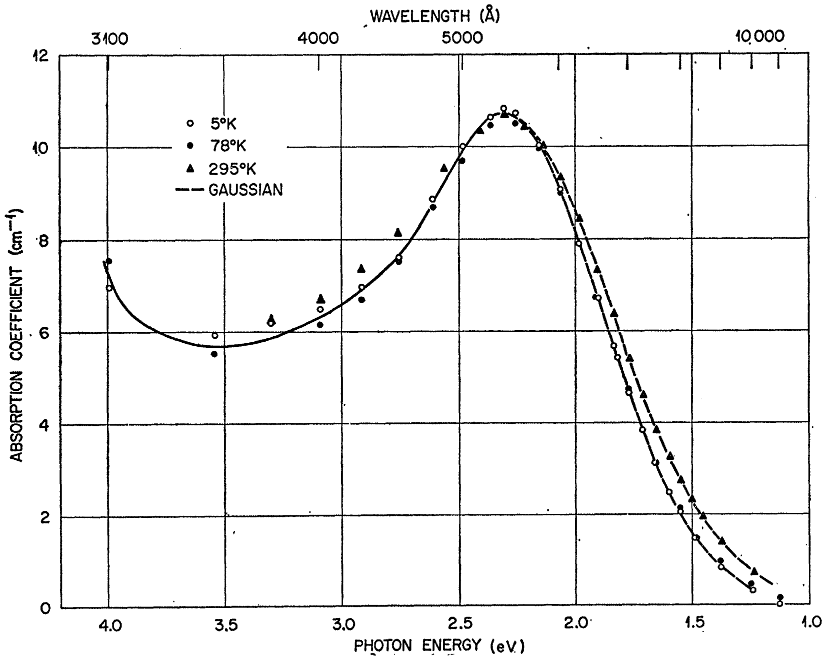

FIG. 2. Absorption spectra of the 2.3-eV band resulting from gamma or electron irradiation at 5, 78, and 295°K. The 295°K data were taken point by point 30 sec after each gamma irradiation.

RESULTS

One of the most prominent absorption bands produced by ionizing radiation in MgO occurs at 2.3 eV. Figure 2 shows the shape of this band at three different temperatures, 5, 78, and 295°K. At 5 and 78°K, if a symmetric Gaussian shape is assumed for the absorption band, the width at half-maximum is 0.96 eV. It was necessary to assume a symmetric band since other absorption bands, primarily due to Fe impurities, are superimposed on the ultraviolet side of the 2.3-eV band. At room temperature the band is slightly broadened with a half-width of 1.07 eV, but the peak position of the band is at 2.3 eV for all three temperatures studied. The concentration of centers responsible for the absorption which can be produced by ionizing radiation reaches a maximum after only a few minutes of irradiation and is the same for all three temperatures. At 5°K the absorption band is stable against thermal decay, while at 78°K a very small decay rate is observed. At room temperature this band decays thermally with a half-life of 2–7 h the rate of decay being sample-dependent. Thus, it was necessary to obtain the shape of the band at room temperature, as shown in Fig. 2, point by point. Each point was taken after a 32°C irradiation of 30 min, which was more than sufficient to saturate the growth of the band, and exactly 30 sec after the specimen was removed from the radiation source.

Figure 3 is a plot of the normalized absorption coefficient, α/α_0, versus time for several specimens irradiated at 32°C and held at 22°C after irradiation. Unfortunately, there was a 30-sec delay after irradiation before the absorption coefficient α could be measured and so α_0, the initial absorption coefficient, was obtained by extrapolation from a graph of α versus time. The curves shown in Fig. 3 are from data taken with samples obtained from the General Electric Company,[19] Muscle-Shoals Electrochemical Company and the UKAERE at Harwell.[20] As can be seen in the figure, there appears to be no definite relation between the rates of decay and the magnitude of α_0.

The centers responsible for the 2.3-eV absorption can be optically bleached at 5°K with filtered light of broad spectrum centered near 540 nm, but we were unable to bleach the centers with either infrared light or light of wavelength 256 nm produced by a high-intensity deuterium lamp in conjunction with an interference filter. Wertz and his collaborators determined from spin-resonance experiments that the 2.3-eV centers, which they labeled V_1, have ⟨100⟩ symmetry.[11] It is of interest, therefore, to determine whether optical dichroism is present in irradiated cyrstals which have been optically bleached with polarized light. We found that, even though specimens were bleached at 5°K with light polarized along either ⟨100⟩ or ⟨110⟩ directions by a Glan-Thompson prism, no observable anisotropy was produced. These results indicate that there is no dichroism along the ⟨100⟩, ⟨110⟩, or ⟨111⟩ directions. However, this does not imply that the V_1 center does not have symmetry axes as indicated by ESR experiments but rather suggests that even at 5°K the lifetime of a hole on any particular oxygen next to the positive-ion vacancy is short compared to the time required for bleaching and measuring.

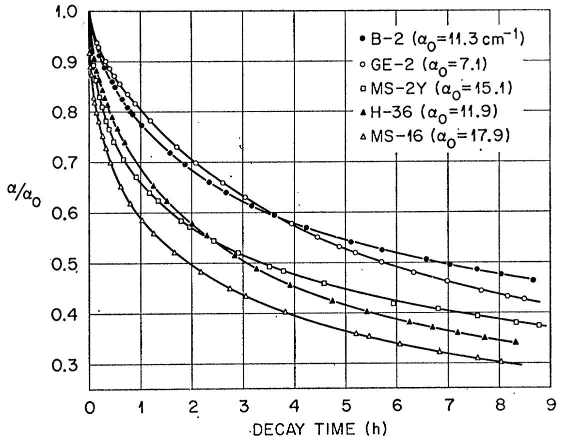

FIG. 3. Room-temperature decay rates of V_1 center in different crystals irradiated to saturation in gamma source. α/α_0 is the fraction of the V_1 absorption that has not decayed.

The concentration of V_1 centers that can be introduced by ionizing radiation is found to be crystal-dependent. The production of this defect is suppressed by doping with certain impurities, such as cobalt, chromium, manganese, and titanium. In undoped crystals, the concentration of V_1 centers that can be introduced is dependent on the thermal treatment of the samples. For example, the total concentration of centers can be suppressed by slow cooling of the specimens from an elevated temperature, say 1000°C; on the other hand, it can be enhanced by quenching from high temperature. In Fig. 4, the absorption coefficient α of the V_1 band is shown as a function of the quenching temperature T_Q for three different crystals. Prior to quenching, each sample was slow cooled individually and then the following procedure was utilized. After 5 min of incubation in argon at a temperature T_Q the sample was withdrawn from the hot zone in the oven by a rod and allowed to drop on to a copper plate. This resulted in a fast quenching rate without thermal fracture of the specimens. The samples were quenched from successively higher temperatures and measured after each quench for the concentration of defects introduced by a 20-min irradiation in the gamma source. Up to a quenching temperature of about 500°C, there was no noticeable increase in the concentra-

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[19] The samples obtained from the General Electric Company were kindly supplied by R. L. Hansler and G. A. Slack.

[20] The crystals obtained from the Atomic Energy Research Establishment at Harwell were kindly supplied by B. Henderson and grown by N. Quinn of W. & C. Spicer Ltd. and J. Burrow of Bristol University.

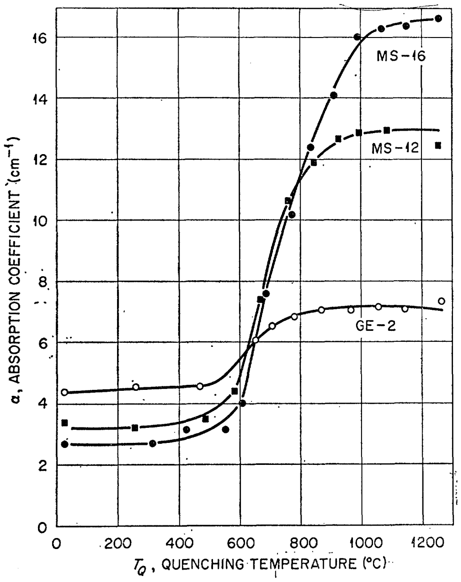

FIG. 4. Absorption coefficient of the 2.3-eV band resulting from gamma irradiation versus the quenching temperature for three samples from different sources. Each sample had previously been slow-cooled to decrease the radiation-induced absorption coefficient.

tion of the centers that could be introduced. At about 500°C, the concentration of the radiation-induced centers began to increase with quenching temperature, and above a still higher temperature, the absorption coefficient became independent of the quenching temperature. This latter saturation temperature is crystal-dependent, and saturation suggests that the total concentration of V_1 centers is governed by the type and amount of impurity present in the crystal.

The effect of quenching on the colorability of the V_1 band in MgO can be eliminated by reheating the sample to about 1000°C and then slow cooling. For example, when a quenched sample with a saturated absorption coefficient of 14 cm^{-1} is cooled from 1000°C at a rate of 20°C per h in argon and then re-irradiated the absorption coefficient reaches a maximum of only 2 cm^{-1}. The process of increasing and decreasing the concentration of these centers by thermal treatment is reversible. Moreover, contrary to previous reports,[4,9] we find that the maximum V_1 concentration is independent of whether samples are incubated in hydrogen, oxygen, argon or in vacuum prior to quenching, for the temperature range up to about 1250°C. Instead the quenching rate determines the concentration of the defects. To illustrate this, crystals were quenched to room temperature in the incubation atmosphere without exposure to air. The region of the tube in which the sample rested was withdrawn from the hot zone of the furnace and cooled rapidly with the aid of a fan. By this means a specimen initially at 1200°C could be cooled to 500°C in 30 sec. For this experiment we used some of our purest crystals, B-3 and B-4, and found that a sample heated in hydrogen atmosphere for 2 h at 1130°C and quenched yielded the same 2.3-eV absorption after irradiation as one treated similarly in argon. (The heat treatment of MgO specimens in hydrogen atmospheres at temperatures much above 1130°C usually resulted in cloudy specimen surfaces.) The sample which was heat-treated in argon was further heat-treated in oxygen under identical conditions for a total of 27 h, five optical measurements were made during this period. While the iron band at 290 nm was observed to increase and saturate during this period, no change in the radiation-induced V_1 concentration was observed. Further heat-treating in oxygen at 1250°C for 5.2 h caused almost no changes in the optical spectrum indicating that a saturation level had been reached. We did find that a sample heated for 2 h at 1210°C prior to quenching in a vacuum of 10^{-5} Torr and then irradiated yielded a 2.3-eV absorption approximately 20% less than that for one heated in oxygen. This is probably due to the difference in quenching rates, since a vacuum quench is much slower than a gas quench.

It was possible to obtain a rough estimate of the oscillator strength of the 2.3-eV band by combining optical and ESR measurements[21] on the same series of crystals. Wertz *et al.*[11] first observed the ESR spectrum of the V_1 center and found that $g_{\|}=2.0032$ and $g_{\perp}=2.0385$. In our experiment four samples were used, three of which were cleaved from the same Muscle-Shoals ingot and one obtained from General Electric Company. After irradiation the Muscle-Shoals crystals varied considerably in absorption coefficient, 2.3 cm^{-1} for a slow-cooled sample, 11.4 cm^{-1} for one quenched in vacuum and 14.5 cm^{-1} for one quenched in oxygen. A quenched GE sample had an absorption coefficient of 7.2 cm^{-1}. The ESR signal for each of the irradiated samples was measured at 78°K and the magnitude of the signal was compared with the optical-absorption data. The total number of spins measured by the spin resonance was obtained by comparing the V_1 center signal with that from a standard sample. The amplitude of the ESR signals correlated fairly well with that of the optical absorption and furthermore optical bleaching of the V_1 band in the GE crystal eliminated the ESR signal. This general agreement establishes further evidence that the 2.3-eV band is the V_1 center determined by ESR. From the data the oscillator strength of this center is estimated to be between 0.1 and 0.2. This probably corresponds to a lower limit of the oscillator strength since the standard sample was calibrated with respect to the amplitude of a Cr signal in a particular MgO crystal, and the concentration of Cr in this crystal was obtained by neutron activation analysis. This measures the *total* concentration of an impurity in a crystal, whereas

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[21] The ESR measurements were made by M. M. Abraham and R. A. Weeks of this laboratory, and we are very grateful for their help and cooperation.

ESR techniques normally detect only that amount of impurity in a particular valence state. This means that the number of spins measured by ESR methods could be less than the total impurity concentration.

We have made a preliminary study of the spontaneous luminescence of irradiated crystals and have found that there are three spectral regions in which luminescent bands appear after irradiation, the near infrared, red, and ultraviolet regions. The samples were irradiated at 32°C and measured at room temperature after a delay of about 1 min. The luminescence intensity was measured as a function of wavelength over the range 200 1100 nm and the spectral response of the multiplier phototube-monochrometer system was calibrated using a quartz-iodine tungsten filament lamp with calibration traceable to the National Bureau of Standards. The data shown in Figs. 5 and 6 illustrating the relative intensities of the luminiscent bands in several crystals have been corrected with respect to wavelength response of the apparatus, but have not been corrected for the thickness or self-absorption of the specimens.

Figure 5 shows the luminescence "afterglow" for several different samples of MgO in the spectral region of 3.0–4.0 eV. The luminescence in this part of the spectrum is strongly affected by self-absorption of the samples caused by Fe impurity absorption above 4 eV and the broad V_1 band absorption below 3 eV. Thus, the amount of self-absorption is crystal-dependent and can result in apparently false peak positions for the luminescence bands. In order to give at least a qualitative idea of the relative magnitude of the self-absorption in the samples, Table I lists the Fe concentrations and

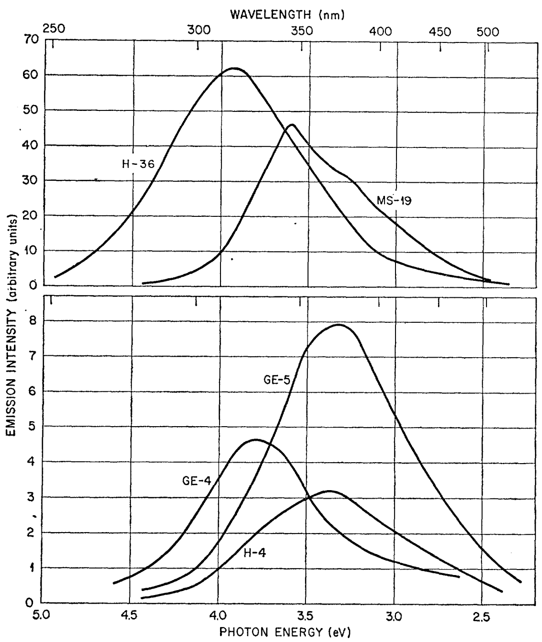

FIG. 5. Room-temperature luminescence afterglow at 2.5–4.5 eV induced by gamma irradiation.

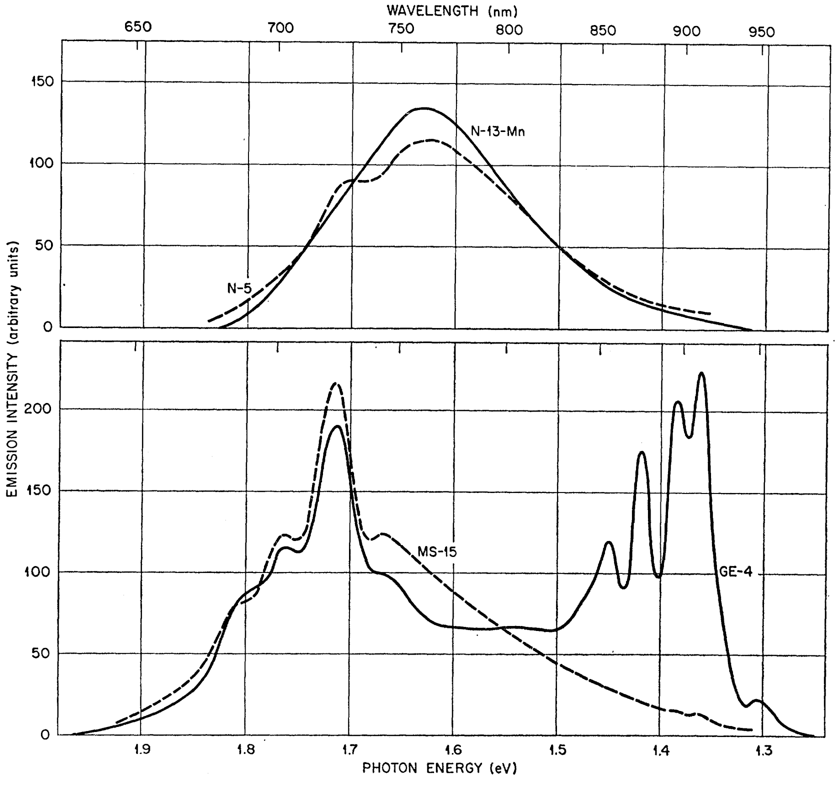

FIG. 6. Room-temperature luminescence afterglow at 1.3–1.9 eV induced by gamma irradiation.

maximum V_1 absorption coefficients for these specimens. Even though it is not possible to accurately identify the peak positions of the luminescence bands, it is still clear from Fig. 5 that there are at least two major peaks in this region. For example, if we consider only the relatively pure crystals, H-36, GE-4, and GE-5, it is evident that a minimum of two bands are necessary to characterize the data.

Some variations of the luminescence in this spectral range are occasionally found even in specimens from the same crystal, e.g., GE-4 and GE-5. This crystal-dependent characteristic suggests that these bands are sensitive to various trace impurities. It was further found that large concentrations (600 ppm) of certain impurities such as cobalt suppress all luminescence between 1.2 and 6.0 eV. Heat-treatments can also alter the luminescent intensity. For a sample quenched from 1000°C, viz., MS-19 in Fig. 5, the luminescent intensity was large following irradiation, whereas if a sample was slow-cooled from the same temperature over a 3-day period, it was undetectable indicating at least a two order of magnitude decrease. Luminescence spectra were also taken on several crystals while they were being irradiated with 230-kV x rays at 15 mA, and it was determined that the afterglow luminescence and that given off during irradiation had the same spectra.

In the spectral region of 1.3–1.9 eV most of the crystals investigated showed a luminescent intensity about an order of magnitude greater than that in the ultraviolet and had a characteristic luminescence similar to that shown for samples MS-15 in the lower portion of Fig. 6 with peaks at about 1.66, 1.72, 1.77, and 1.81 eV. However, there are notable exceptions. Several crystals obtained from the Norton Chemical Company gave as primary luminescence a broad band centered at about 1.63 eV. This band seemed most pronounced in a sample doped with manganese[22] and the spectra of this sample and an undoped Norton specimen are shown in the top part of Fig. 6. Moreover, slow-cooling a sample from 1000°C resulted in about a factor of 2 less luminescence intensity than that for a similar sample which had been quenched.

In some of the MgO crystals investigated a series of luminescence bands was detected in the region of 1.4 eV. The peak positions of about 1.362, 1.384, 1.418, and 1.450 eV and the relative intensities of the peak heights for the samples are always the same, suggesting interaction of lattice vibrations with an optical transition. It was found that these bands could be quenched by cooling the sample to 78°K. If a specimen is irradiated at 305°K, cooled to 80°K and the afterglow observed, the bands are not detectable. Upon warming, the bands appear and then decay rapidly. With the exception of these luminescence bands, all those considered above decay at 78°K as well as room temperature at rates much faster than those observed for the V_1 absorption at room temperature.

DISCUSSION

Wertz and his collaborators[4] were able sometime ago to tentatively link the 2.3-eV optical absorption band produced by ionizing radiation in MgO with a defect center detected by ESR techniques which they had identified as a hole trapped at a positive-ion vacancy. Our results confirm their correlation of the ESR signal and the optical absorption. However, the identification of the center as a positive-ion vacancy with a trapped hole still hinges on their ESR work. We shall consider that the 2.3-eV band is due to these V_1 centers and discuss our results from this point of view.

In order to form the V_1 center two entities are required: holes and positive-ion vacancies. Electron-hole pairs are generated in the lattice by radiation and the concentration of these pairs at any instant is governed by the radiation intensity and the concentration of the impurity recombination centers. Positive-ion vacancies can be created in several ways. Since MgO is primarily ionic, a detailed balance of the electrostatic charges of the defects is necessary. If a substitutional impurity such as Fe is present in the valence state Fe^{3+} then since each indigenous cation site has a 2^+ charge there must exist one positive-ion vacancy for every two Fe^{3+} ions in order to maintain electrical neutrality. If on the other hand, the Fe is present in the lattice as Fe^{2+} no positive-ion vacancies are needed to balance their charge. It is known that impurities can be incorporated into MgO crystals in different valence states and Groves and Fine[23] have shown that the valence state of Fe in MgO can be altered by certain heat treatments. This means that it should be possible to change the concentration of positive-ion vacancies in a specimen simply by the proper heat treatment. Positive-ion vacancies can also be introduced into the crystal by deformation or by the quenching-in of Schottky defects, that is, positive and negative-ion vacancy pairs, from high temperatures. Another possibility of increasing the positive-ion vacancy concentration is through the quenching-in from high temperatures of interstitial-vacancy pairs, or Frenkel defects. In principle an estimate can be made on the basis of the relative formation energies as to whether Schottky of Frenkel defects are more favorable in MgO at high temperatures[24,25] but an accurate calculation is formidable. The implication of the possibilities discussed above is that if positive-ion vacancies are responsible for the formation of the 2.3-eV absorption band, from a careful study of the effect of heat treatment on the formation of V_1 and F centers

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one should be able to distinguish whether impurity-induced vacancies, Schottky defects, or Frenkel defects are the more likely source of vacancies in the crystal.

There is little doubt that certain impurities can act as recombination centers for electrons and holes in MgO and thus reduce the concentration of hole centers that can be formed. We find that in specimens doped with Mn, Ti, Co, and Cr the production of V_1 centers is completely suppressed, and in the case of 600-ppm Co-doped crystals all luminescence is likewise suppressed. On the other hand, specimens from Muscle-Shoals containing 50 ppm Fe gave as many V_1 centers and often more than did purer samples. These results are explicable in terms of the relative capture cross section of the impurities for holes. From our results Co seems to be an effective hole trap, whereas Fe is not as effective.

We now turn our attention to whether impurity-induced cation vacancies, Schottky defects or Frenkel pairs determine the maximum concentration of V_1 centers that can be produced. If either Frenkel or Schottky defects were responsible for the observed V_1 concentrations, then quenching from increasingly higher temperature should result in more V_1 centers; but as shown in Fig. 4, all the samples tested show a saturation behavior for quenching temperatures above 1000°C. Conceivably this saturation could be due to an inability to quench-in high-temperature lattice defects because of the finite quenching rate used, but note that in Table I the thickest sample showed the largest V_1 center saturation value. This suggests that the quenching rate was sufficient to quench-in the defects that were present and that neither Schottky nor Frenkel defects are responsible for the V_1 centers observed. Furthermore, if Schottky defects were responsible for the V_1 coloration, one would expect as many F as V_1 centers and no F centers were detected at 250 nm.[2]

If the V_1 coloration is not due to Schottky or Frenkel defects, then perhaps a combination of electronic processes and impurity-induced vacancies is responsible. It has been previously reported that the formation of V_1 centers can be greatly enhanced by heat treating a crystal in oxygen at 1200°C or more.[4,9] We find, however, the V_1 concentration is strongly dependent on the quenching rate, and that oxygen heat treatment has no effect on the maximum V_1 concentration. Heat treatment of a sample at 1000°C in hydrogen, argon, or oxygen atmospheres followed by a quick quench and 30 min of ionizing radiation results in the same V_1 concentration. If a sample is heat treated in vacuum, there is a slight decrease in the V_1 concentration that can be produced; but this is most likely due to the reduced quenching rate in the evacuated chamber. Slow cooling a previously quenched crystal from 1000°C in any atmosphere results in a substantial decrease in the maximum V_1 center concentration. These results are not unreasonable if the electron-hole trapping capabilities of impurities can be altered by heat treatment or if slow cooling results in fewer positive-ion vacancies.

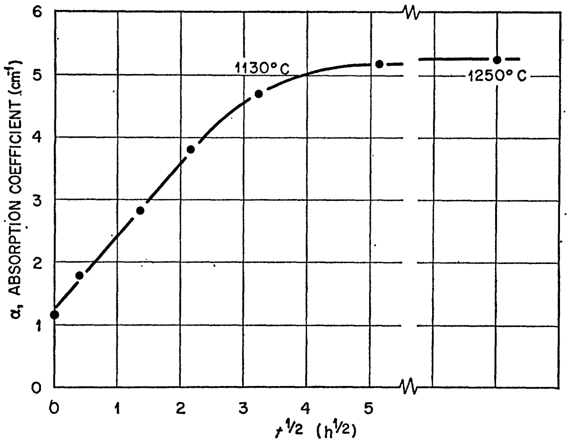

FIG. 7. Increase in the absorption coefficient at 290 nm versus the square root of the incubation time in oxygen atmosphere at 1130°C. The effect of further heat treatment for another 5.2 h at 1250°C is shown at the right of the figure.

Groves and Fine[23] have indicated that exposure of Fe-doped MgO crystals to high temperatures result in a large amount of the iron being present as Fe^{3+}. Weber[26] has also shown that the 4.3-eV absorption band in MgO, which has been attributed to Fe^{3+} centers,[9,10] increases when crystals are heated in an oxygen atmosphere to high temperature. He found that the increase in the absorption coefficient of this band was proportional to the square root of the time for which the sample was held at temperature in oxygen and obtained a diffusion coefficient at 1200°C of $D \approx 0.2 \times 10^{-7}$ cm^2/sec. We have duplicated his work and Fig. 7 which depicts the increase in absorption coefficient at 4.3 eV as a function of the square root of the incubation time shows that our results are very similar to Weber's. We arrive at a value of $D \approx 0.4 \times 10^{-7}$ cm^2/sec at 1130°C. Both of these diffusion coefficients are orders of magnitude greater than those determined for either intrinsic or extrinsic oxygen diffusion in MgO.[27,28]

Since two Fe^{3+} ions can be expected to result in one positive-ion vacancy, a quenched crystal containing predominately Fe^{3+} might be expected to have a higher potential V_1 concentration than a slow-cooled crystal which contained mostly Fe^{2+}, but there appears to be no correlation between the V_1 concentration and the Fe^{3+} band height at 4.3 eV. Whereas the V_1 concentration in a crystal is dependent on the quenching rate and not on the atmosphere at which the heat treatment is carried out, the Fe^{3+} concentration increases with

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oxygen and decreases with hydrogen treatment. This suggests that the valence state of the Fe impurity is not effective in influencing the production of V_1 centers. Furthermore, a comparison from Table I of the maximum V_1 concentration produced in the various crystals investigated with total Fe impurity suggests that the Fe concentration has little to do with V_1 production. In fact, it appears that in the purer crystals such as those from General Electric, Harwell, and Bristol, the V_1 concentration as determined from ESR measurements is as much as three times greater than the expected impurity-induced positive-ion vacancy concentration in the crystal assuming all the Fe and Cr impurities to be in the trivalent state. However, the difficulties in obtaining accurate concentrations of V_1 centers from ESR data and impurities from chemical analyses are great and make our comparison somewhat inexact. In light of these results it appears that electronic processes such as electron-hole trapping and recombination may be more important in determining the production rate of V_1 centers than ionic processes that involve association of defects and detailed charge balancing.

The possibility that deformation debris in the samples are responsible for the V_1 coloration must also be considered. All of the crystals investigated were grown by arc-fusion techniques and thus were quenched from temperatures above 2500°C. This treatment obviously results in the formation of many dislocations, as can be seen from the etch-pit studies of Stokes and Li[29] and Rovner and Rhodin,[28] and a great deal of dislocation debris such as dipoles. Such dislocation debris increase the colorability of KCl crystals[30] and might be expected to do the same in MgO. We deformed a slow-cooled MgO crystal as much as 4% and found little or no increase in V_1 center absorption after irradiation. However, the crystals are probably already so heavily deformed by the growth process that our result is not very meaningful. A careful study of the colorability of samples annealed at 2000°C for several hours and subsequently deformed should be made.

Another interesting aspect of the absorption data is the observed thermal decay of the 2.3-eV band at room temperature. The decay of this band must be attributed to either the hole leaking off the positive-ion vacancy and being trapped or annihilated at some other site or electrons being released from shallow traps and recombining with the hole at a V_1 site. If the latter process was solely responsible for the spontaneous loss of V_1 centers at room temperature, then a plot of absorption coefficient versus time at room temperature should be impurity-dependent. If the former process was dominant, then this plot should depend on the initial V_1 concentration. Figure 3 indicates that there is no clear-cut dependence either on the initial V_1 or the Fe impurity concentration. This leads us to believe that the decay is due to both processes in the crystals investigated.

It is not possible at this time to say much about the radiation-induced luminescence data. All of the bands decay at room temperature about two orders of magnitude faster than the 2.3 absorption band, and even at 5°K they disappear rapidly after irradiation. We have not been able to correlate the V_1 center with any of the luminesecnce bands observed.

In summary we conclude that ionizing radiation in MgO produces changes in the impurity states of the crystal and can create other defects such as the V_1 center. It has been possible to show that the 2.3 eV optical absorption created by radiation is connected with a center studied by Wertz and his collaborators by means of ESR. The production of the V_1 band by radiation is impurity-dependent and, perhaps more important, depends markedly on the thermal treatment of the crystal. Further, there appears to be no correlation between the iron concentration and the V_1 concentration.

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