

Photoconversion of F -type centers in thermochemically reduced MgO single crystals

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Optical absorption and luminescence experiments were used to study the photoconversion of neutral oxygen vacancies (F centers) in MgO single crystals thermochemically reduced at elevated temperatures. In crystals with an undetectable concentration of hydride ions and a moderate concentration of F centers ($\approx 10^{17}$ cm $^{-3}$), excitation with UV-light produces positively charged anion vacancies (F^+ centers) and electrons which are subsequently trapped at impurities. Under continuous excitation, the F^+ centers release holes which are trapped at cation vacancies charge compensated by impurities. In crystals with high concentrations of both hydride ions and F centers ($\approx 10^{18}$ cm $^{-3}$), the electrons from the F to F^+ photoconversion are trapped mainly at the hydride ions to form H^{2-} ions, which are metastable at room temperature. [S0163-1829(99)12101-5]

I. INTRODUCTION

Magnesium oxide is a simple oxide with fcc structure and a melting temperature in excess of ~ 3073 K. The band gap is 7.8 eV. Point defects produced in this material can be characterized by their optical properties.¹ Defects in the form of vacancies can be produced by two methods. The first is by irradiation with energetic particles, such as neutrons, electrons, and ions. The second is by thermochemical reduction (TCR), performed under strongly reducing conditions at high temperatures, resulting in stoichiometric deficiency in the oxygen sublattice. The deficiency results in isolated anion vacancies.

In an earlier study,² we addressed the photoconversion of the two charge states of the anion vacancies in neutron irradiated MgO: F^+ and F centers, which are oxygen vacancies with one and two electrons respectively. The superscript refers to the net charge on the defect. In MgO both the F^+ and the F centers absorb essentially at the same energy: 4.92 and 5.01 eV, respectively.³ However, their photoluminescence peak at 3.2 and 2.3 eV, respectively.^{3,4} In the present work, we investigate photoconversion of anion vacancies in TCR crystals.

The major differences in anion-vacancy properties between neutron irradiation and TCR are as follows: In neutron-irradiated anion vacancies are normally in the F^+ state.⁵ The vacancies are stable up to about 400 K, above which interstitials begin to be mobile and recombine with the

vacancies.⁶ In TCR crystals the anion vacancies prefer to be in the F state. When a TCR sample is placed on a hot plate (>450 K), any F^+ centers present become exclusively F centers.⁷ Since these vacancies are produced nonstoichiometrically, there are no interstitials to annihilate the vacancies. Therefore the F centers are stable even at very high temperatures, ~ 1100 K.^{6,8} However, the production of anion vacancies by TCR is normally also attended by the H^- ion,⁹ which is a proton trapped at a double-negative anion vacancy site and is therefore positively charged. Since MgO crystals contain hydrogen to a greater or lesser extent, TCR results in both anion vacancies and H^- ions. The H^- configuration is thermally more stable than anion vacancies, at least 1900 K in some situations;⁸ this indicates that the proton renders the anion vacancy it occupies greater stability. The presence of H^- ions affects the optical and photoconversion properties of anion vacancies in MgO.¹⁰⁻¹² In the present work, we shall provide the big picture involved in the photoionization process of anion vacancies with and without the presence of the H^- ions.

Another important difference between neutron-irradiated and TCR crystals is the effect resulting from photoexcitation of anion vacancies. As we have seen, in neutron-irradiated crystals holes can populate existing impurity-compensated cation vacancies to give rise to optically active V -type centers, which absorb at 2.3 eV. In the case of TCR crystals the creation of nonstoichiometric excess of anion vacancies is compensated by the nonstoichiometric deficiency of cation vacancies, governed by the mass-action law. Therefore in

TCR crystals, *V*-type centers become less of a factor as the concentration of anion vacancies increases.

II. EXPERIMENTAL PROCEDURES

The MgO crystals used were grown at the Oak Ridge National Laboratory using the arc fusion technique.¹³ The starting material was MgO powder from the Kanto Chemical Company, Japan. TCR was performed in a tantalum chamber at ~ 2000 K and ~ 7 atmospheres of magnesium vapor, followed by rapid cooling. This process produces anion (oxygen) vacancies, due to a stoichiometric excess of cations. If hydrogen impurities are present in the crystals, they can be trapped at these vacancies forming H^- ions.⁹ Prior to optical measurements, samples were annealed for 10 min at 900 K in flowing nitrogen.

The spectrophotometer used in the UV-VIS-IR region was a Perkin-Elmer, Lambda 19 spectrophotometer. Far infrared data were taken with a Perkin-Elmer 2000 FT-IR spectrophotometer. The sample was excited with a low-intensity 5.0 eV light, the source being a 50-W Hg lamp in conjunction with a 7200 Oriel monochromator set at 250 nm. The emitted light was focused into the entrance slit of a SPEX 1000M monochromator and detected with a Hamamatsu R943-02 cooled photomultiplier. The spectra were recorded with a SR400 gated photon counter. For low-temperature measurements, the samples were placed inside a quartz cryostat filled with liquid nitrogen.

III. RESULTS AND DISCUSSION

Two types of TCR MgO crystals were used: with undetectable and detectable H^- ions. Samples A and B had an undetectable concentration of H^- ions and *F*-center concentrations of 1×10^{17} and 4×10^{17} cm^{-3} , respectively. Sample C had a concentration of H^- ions of 2.6×10^{18} cm^{-3} and a *F*-center concentration of 1.5×10^{18} cm^{-3} . Undetectable H^- concentration means 10^{16} cm^{-3} or less. From previous studies, we know that 10^{16} H^- concentration is still sufficiently large to affect the optical properties of anion vacancies.^{10,14} Even though infrared absorption cannot determine H^- concentration below 10^{16} cm^{-3} , there are two sensitive ways to gauge a rough estimate: photoluminescence and phosphorescence. These will be addressed.

In photoluminescence, in the absence of H^- ions ($< 10^{14}$ cm^{-3}), F^+ luminescence dominates;¹² in the presence of a small amount of H^- ions, *F* emission dominates.¹² Even a small concentration of H^- ions, $\sim 10^{15}$ cm^{-3} , would result in a green phosphorescence readily detectable by the eye.¹² In a crystal in which protons were removed prior to TCR, the photoluminescence was the F^+ and there was no phosphorescence.¹²

A. Anion vacancies with undetectable H^- ions

The principal crystal used (Sample A) had a *F*-center concentration of 1×10^{17} cm^{-3} and undetectable H^- ions. The former was calculated from the absorption coefficient at 4.95 eV.¹⁵ The absorption spectra before and after excitation with 5.0 eV light are shown in Fig. 1. The peak remained essentially at 5.0 eV. There were some changes in the spectra, reflecting conversion from *F* to F^+ state at 5.0 eV and

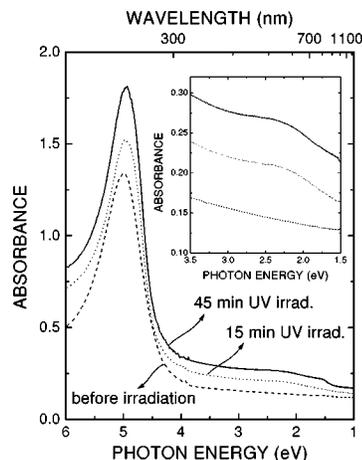
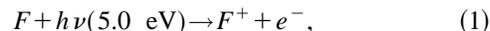


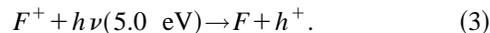
FIG. 1. Optical-absorption spectra of a thermochemically reduced MgO crystal (Sample A) after annealing for 10 min at 900 K and after subsequent UV irradiation. The sample thickness was 1.1 mm. The inset is an enlargement of the 3.5–1.5 eV region.

impurity-related defects in the background. In the inset is shown an expanded absorbance indicating the presence of the 2.3 eV band. This band is attributed to *V*-type centers, due to holes trapped at cation vacancies compensated by Al^{3+} , F^- , and OH^- impurities.^{16,17} The *V* concentration, based on the oscillator strength¹⁶ of 0.05 and a full width at half maximum of 1.1 eV, is estimated to be 7×10^{16} cm^{-3} . In virgin MgO crystals the concentration of *V*-type centers is typically $\sim 10^{17} - 10^{18}$ cm^{-3} . As pointed out in the introduction, in TCR crystals, it is expected that these vacancies would be suppressed in conformity with the mass-action law; an increase of anion vacancies correspondingly decreases cation vacancies. As a verification, Sample B with a fourfold higher *F* concentration (4×10^{17} cm^{-3} and undetectable H^- ions) yielded no 2.3 eV absorption.

Initially, Sample A contained *F* centers and iron impurities in the Fe^{2+} state. Upon bleaching, the following reactions take place:⁷



With continuous excitation the newly formed F^+ centers would release holes according to the reaction



The release holes would then be trapped by cation vacancies compensated by Al^{3+} , F^- , and OH^- impurities via the processes



where the linear configurations are $Al^{3+} - O^{2-} - [Mg \text{ vacancy}] - O^-$; $Mg^{2+} - F^- - [Mg \text{ vacancy}] - O^-$; and $Mg^{2+} - OH^- - [Mg \text{ vacancy}] - O^-$, respectively.¹⁸ The O^-

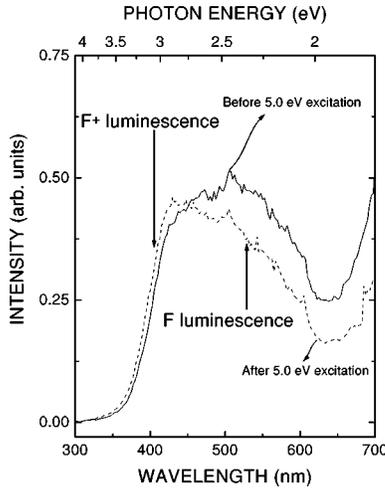


FIG. 2. Photoemission spectra of Sample A before (solid line) and after (broken line) excitation with 5.0 eV light. The crystal thickness was 1.1 mm.

ion represents an O^{2-} ion with a trapped hole. All three trapped-hole centers absorb at 2.3 eV.^{16–18}

Heating at $T \approx 900$ K for several minutes, the UV-irradiated crystal returned to its original F state, and the optical absorption band at 2.3 eV disappeared indicating that holes from the V -type centers have escaped. Thus, formation and annihilation of these trapped-hole centers is a reversible process and the crystal can be cycled between these states repeatedly.

To distinguish F^+ from the F centers, we used optically excited luminescence. The luminescence obtained by exciting with 5.0 eV photons is shown in Fig. 2. The luminescence was primarily due to F centers, with a small F^+ component. We note that with prolonged excitation, the F luminescence appeared to have diminished. The decrease is not due to a decrease in F emission, but due to self-absorption of the F luminescence incurred by the build-up of V -type centers. Both the V -type absorption and the F luminescence peak at ~ 2.3 eV. In brief, starting at thermal equilibrium (with F centers, Fe^{2+} ions, and no trapped-hole centers) excitation with 5.0 eV photons has the net effect of transferring a positive charge from Fe^{2+} to form a trapped-hole center.

There was a green phosphorescence of a few seconds after excitation with 5.0 eV light. The existence of the phosphorescence indicates that there was a small amount of H^- ions, albeit not measurable by absorption. This is due to the thermal release of an electron from the metastable H^{2-} ion.¹⁹ Since Sample B also had less than 10^{16} H^- ions cm^{-3} , we used phosphorescence to gauge the presence of H^- ions. The phosphorescence was of the order of a minute, indicating that the concentration was higher than in Sample A. The photoluminescence was also primarily F center (see Fig. 3). There was no decrease of the F emission with prolonged irradiation, since there were no V -type centers formed.

B. Anion vacancies with H^- ions

1. Absorption

The TCR sample used contained 1.5×10^{18} F centers/ cm^3 and 2.6×10^{18} H^- ions/ cm^3 (Sample C). The latter was

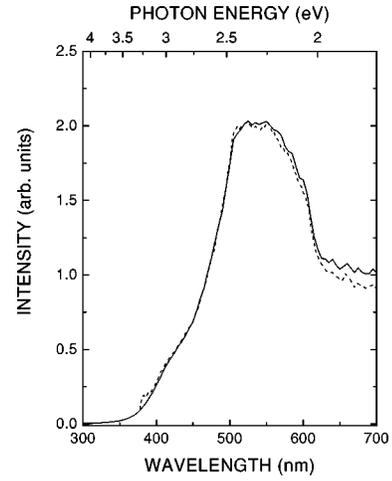
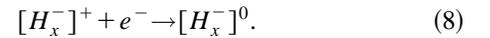
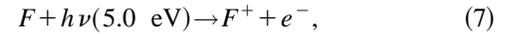


FIG. 3. Emission spectra of a thermochemically reduced MgO crystal (Sample B) before (solid line) and after (broken line) excitation with 5.0 eV light. The crystal thickness was 0.75 mm.

obtained⁸ from the infrared spectrum shown in Fig. 4. Excitation with 5.0 eV photons at 77 K created a broad absorption band at 3.0 eV (Fig. 5). With prolonged excitation the absorption grew. This band has been attributed to the H^{2-} ion, which is an H^- ion that has trapped an electron. The process can be described by electronic transition of an H^- complex containing an electron ionized from the F center.¹⁹ This complex has been denoted $[H_x^-]^0$, where the subscript x refers to the perturbing species and the superscript after the bracket to the net charge of the complex.



Excitation at 295 K did not produce the 3.0 eV band (not shown), indicating that the energy level of the $[H_x^-]^0$ complex is sufficiently close to the conduction band that it is unstable at 300 K.

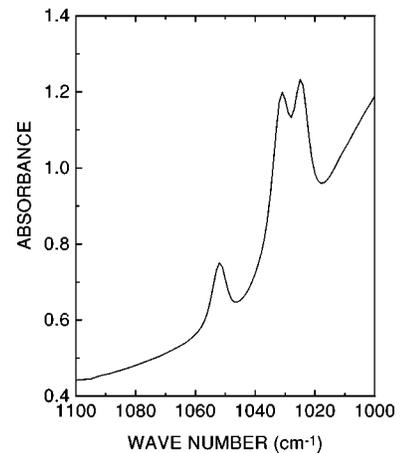


FIG. 4. Infrared-absorption spectrum for H^- ions of the high-hydrogen TCR MgO crystal (Sample C). The crystal thickness was 0.47 mm.

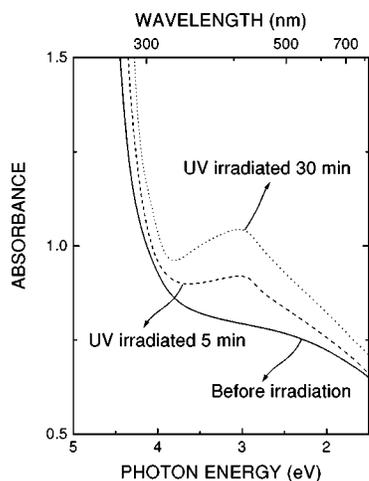


FIG. 5. Optical-absorption spectra of sample C before and after excitation with *F* light.

2. Photoluminescence

Excitation with 5.0 eV light at 295 K produced primarily the *F* luminescence, shown at the top of Fig. 6. Prolonged excitation produced no changes. The bottom of Fig. 6 showed the spectra of the same crystal also at 295 K when placed in a quartz cryostat. Some effects due to the cryostat can be seen in the neighborhood of 350–470 nm. At 77 K the emission intensity decreased by a factor of 6 at the *F* emission peak. With extended excitation with 5.0 eV light, the luminescence intensity decreased. We attribute the decrease to self-absorption of the $[H_x^-]^0$ complex ion which grew with excitation time, as noted in Fig. 5.

3. Phosphorescence

The electron trapped by $[H_x^-]^+$ to form $[H_x^-]^0$ at 78 K [Eq. (8)] is released thermally when the sample is slowly warmed to RT. At 240 K (Refs. 10 and 19) long-lived green thermoluminescence (2.3 eV) is given off. At room temperature, the electrons captured by H^{2-} ions continue to be thermally released, giving rise to green phosphorescence. The intensity and the duration of the phosphorescence provide a measure of the concentration of H^- or H^{2-} ions.¹⁴ Therefore phosphorescence is an extremely sensitive way to determine concentrations of H^- ions below the optical absorption limit of 10^{16} H^- ions/cm³. In the present set of samples, sample A has a phosphorescence lifetime of a few seconds, sample B about a minute, and sample C about 20 min. Therefore, we know that the concentration of the H^- ions was greatest in sample C and least in sample A.

It may be argued that if the concentration of H^{2-} ions is sufficiently high, it is possible to measure the absorption coefficient. This is not possible because at room temperature the probing light beam will quickly excite the electrons from the H^{2-} ions to the conduction band, completely depleting the electrons.

IV. SUMMARY AND CONCLUSIONS

The results of this investigation in thermochemically reduced MgO crystals indicate that: (1) For samples with an

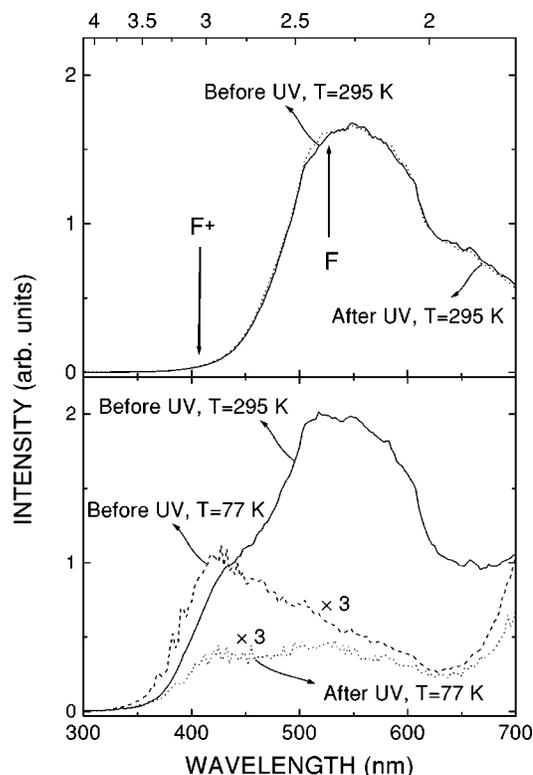


FIG. 6. Emission spectra of Sample C. Top: before and after UV irradiation at 295 K. Bottom: Emission spectra taken in a quartz cryostat before UV irradiation at 295 and 77 K, and after UV irradiation at 77 K. The two spectra recorded at 77 K are enlarged by a factor of 3.

undetectable concentration of H^- ions ($\leq 10^{16}$ cm⁻³) and a moderate concentration of *F* centers ($\approx 10^{17}$ cm⁻³), excitation with UV-light produces positively charged anion vacancies (*F*⁺ centers) and electrons which are subsequently trapped at impurities, mainly Fe²⁺. Under continuous excitation, the *F*⁺ centers release holes which are trapped at cation vacancies charge compensated by Al³⁺, F⁻, and OH⁻. Heating at $T \approx 900$ K anneals out the *V*-type centers and the crystal returned to the original *F* state. (2) No *V*-type centers were observed in a crystal with a higher concentration of *F* centers ($\approx 4 \times 10^{17}$ cm⁻³), in accordance with the mass-action law. (3) In crystals with high concentrations of both hydride ions and *F* centers ($\approx 10^{18}$ cm⁻³), the electrons from the *F* to *F*⁺ photoconversion are trapped mainly at a hydrogen complex denoted as $[H_x^-]^+$ to form $[H_x^-]_0$ ions, which are metastable at room temperature.

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