

Diffusion of Deuterium and Hydrogen in Rutile TiO_2 Crystals at Low Temperatures

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(Received 29 May 1984)

It is demonstrated that diffusion of deuterons and protons in crystalline rutile, TiO_2 , can be induced near room temperature by breaking of the O-H bond with electron irradiation and sweeping of these hydrogenic species along the c axis by an electric field.

PACS numbers: 66.30.Jt, 61.80.Fe, 78.50.Ec

The presence of hydrogen in crystalline oxides can sometimes be detrimental for certain applications. For example, thermochemically reduced crystalline oxides containing isolated oxygen vacancies are ideal candidates as hosts for tunable lasers because these vacancies are thermally stable and emit broad-wavelength luminescence with high quantum efficiencies.^{1,2} However, the lifetimes of the luminescence are too long, as exhibited by MgO , CaO , and Al_2O_3 crystals. The cause of the long-lived luminescence was recently found to be the presence of H^- ions, which are protons in the anion sublattice, each attended by two electrons.^{1,3} The removal of protons inherently present in these crystals eliminates this obstacle.

Protons and deuterons normally diffuse in or out of crystalline oxides only at elevated temperatures. This communication reports a method which enhances diffusion of these hydrogenic species at unusually low temperatures, such as near room temperature. This method has the important advantage of controlling such diffusion in materials which cannot be exposed to elevated temperatures without structural complications, such as phase change, dislocations, grain boundaries, precipitation of impurities, or change of stoichiometry. It involves ionizing radiation by electrons, attended by electric-field sweeping of these species.

It has been shown that protons (or deuterons) can be swept out of a crystalline oxide with open channels (quartz),^{4,5} as well as other oxides (MgO and LiNb_3),^{6,7} at elevated temperatures by use of an electric field.^{4,5} It is proposed here that protons can be removed from an oxide at low temperatures by an electric field if a mechanism is available to break the O-H bond. Such a mechanism is provided by electron radiation, as demonstrated in an earlier study⁸ on MgO crystals in which protons migrated from substitutional OH^- ions to form $\text{Mg}(\text{OH})_2$ precipitates as a result of ionizing radiation through a process referred to as radiation-induced diffusion. The cross section for such a pro-

cess is a phenomenally large 10^8 b at room temperature and 10^6 b at 85 K, which are many orders of magnitude larger than the 0.1 b for the displacement of indigenous ions by elastic collisions.⁹ It is expected that the cross section for the dissociation of OH^- ions in other oxides is comparable in magnitude. The general types of ionization-enhanced motion of muons (presumably also of protons and deuterons) have been discussed by Stoneham.¹⁰

Rutile (TiO_2 crystal) was chosen for demonstration of the feasibility of hydrogen (or deuterium) diffusion at low temperatures enhanced by radiation- and electric-field-induced diffusion (REID) because it possesses a large open channel for easy diffusion. The low activation energy for hydrogen diffusion along the c axis (c_{\parallel} direction) makes it ideal for such a study. In the Arrhenius equation, $D = D_0 e^{-E/kT}$, where D is the diffusion coefficient, the activation energy E is 0.59 eV in the c_{\parallel} direction and 1.28 eV in the c_{\perp} direction.¹¹ The presence of protons and deuterons in the samples was identified by OH^- and OD^- infrared absorption bands at 3277 and 2437 cm^{-1} , respectively.^{11,12} Deuterons were used as the diffusing species in order to distinguish it from proton contamination from the atmosphere or electrical contacts.

The crystals, obtained from Commercial Crystal Laboratory, South Amboy, New Jersey, were cut with the largest surface normal to the direction for c_{\parallel} or c_{\perp} diffusion. They were subsequently chemically polished¹³ in concentrated KOH at about 700 K and then deuterated for 3 h at ~ 1200 K in D_2O vapor, with a partial pressure of oxygen to prevent chemical reduction.¹¹ The sample thickness in all cases was between 1.0 and 1.1 mm. Electrical contacts were made on both faces of a sample with use of a gold-platinum ink A-3395 from Engelhard Corporation. The sample was supported vertically on the edge by a vise with an indium metal contact on one side (negative electrode), and mica on the other. Connection with the positive terminal of the sample was made with a wire spring contact. Irradi-

ations were carried out with a 2.0-MeV Van de Graaff generator with beam intensity maintained at $8\text{--}9 \mu\text{A}/\text{cm}^2$. The sample temperature varied between 340 and 390 K depending on how much air was blown on the sample to prevent excess heating. The electrical field was varied from 200 to 3000 V/cm.

Figure 1(a) shows the spectrum of a c_{\parallel} crystal prior to the REID. The crystal contained primarily OD^- and very little OH^- ions. After REID for 1 h at 340 K with a field of 2000 V/cm, it exhibited the spectrum shown in Fig. 1(b). Approximately half the deuterons had vanished and the OH^- absorbance increased, presumably because of indiffusion of protons from the gold-platinum contacts and/or atmosphere. After another hour of REID, virtually all the deuterons were removed and the concentration of OH^- ions increased further [Fig. 1(c)], suggesting replacement of the deuterons. Hence, under this condition, out-diffusion of deuterons occurred at the effective rate of about 0.5 mm/h.

The same experiment was carried out in a c_{\perp} direction. Some loss of OD^- absorbance was observed, but the out-diffusion rate was less than 5% of that in the c_{\parallel} direction. This anisotropy is compatible with results from earlier studies^{11,14} and the proposed mechanism for hydrogen diffusion in TiO_2 .¹⁵

REID of deuterons under the same electric field was also performed at a higher temperature. By

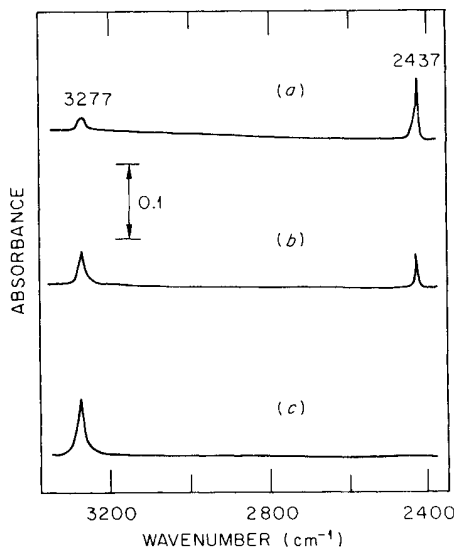


FIG. 1. Infrared absorption spectra of a c_{\parallel} TiO_2 crystal (a) after deuteration in D_2O for 3 h at ~ 1200 K, and subsequent irradiation with electrons with an applied field of 2000 V/cm for (b) 1 h and (c) 2 h.

slowing down the air blowing on the sample, the temperature of another c_{\parallel} sample was determined to be ~ 390 K. At this temperature the rate of D^+ removal was twice as fast. There was one other notable difference: The deuterons were not replaced by protons. A profile of the D^+ concentration was performed along the thickness of a crystal after 80% of the deuterons had been removed; consecutive 0.1-mm increments were removed from the cathode side by abrasion on SiC impregnated paper followed by mechanical polishing. The results showed unambiguously that deuterons were concentrated near the cathode, indicating that the deuterons migrated toward the negative electrode.

Radiation- and electric-field-induced diffusion of deuterons with a field of 2000 V cm^{-1} was also performed on a c_{\parallel} crystal with ^{60}Co γ rays with a flux of $1.4 \times 10^6 \text{ R/h}$.¹⁶ After 10 d, or a total dose of $2.5 \times 10^8 \text{ R}$, there was no loss of deuterons.

Electric field dependence of REID on D^+ out-diffusion was also performed. Several c_{\parallel} samples were irradiated at 360 K for 30 min each. The results are plotted in Fig. 2. It can be seen that a strong field effect was observed. Field strengths of less than 1000 V/cm are not very effective in enhancing D^+ out-diffusion.

For comparison, out-diffusion of deuterons was performed without the irradiation. Deuterated c_{\parallel} crystals were heated isochronally for 30 min under an electric field of 2000 V/cm. No loss of deuterons was observed below 450 K. A temperature in excess of 550 K was needed in order to remove half the deuterons.

The results from REID can be compared with the corresponding deuteron removal rates obtained

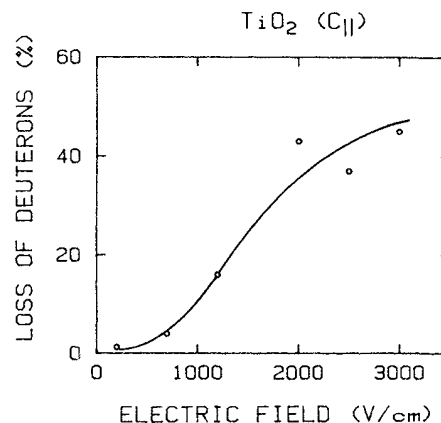


FIG. 2. Loss of OD^- absorbance (in percent) vs electric field strength. Each sample was irradiated for 30 min.

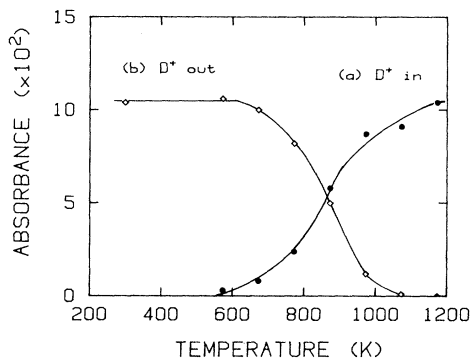


FIG. 3. Absorbance vs annealing temperature for (curve *a*) isochronal in-diffusion of deuterons from D_2O vapor and (curve *b*) isochronal out-diffusion of deuterons in O_2 gas.

from a purely thermal out-diffusion. Figure 3 shows the in-diffusion (curve *a*) and subsequent out-diffusion (curve *b*) of deuterons. A sample was deuterated isochronally (30 min each) at increasing temperatures. The OD^- absorbance increased with increasing temperatures. After the final D^+ in-diffusion at $T = 1173$ K, out-diffusion of the deuterons was performed, also isochronally (30 min) at increasing temperatures, but in flowing oxygen. It is noted that removal of most of the deuterons is achieved only near 1000 K. With use of REID, complete removal can be obtained in comparable times at 340 K.

On the basis of the present work, it is proposed that diffusion of protons (and perhaps even other light impurity ions) can be induced in other oxides with use of REID.

This research was sponsored by the Division of Materials Science, U. S. Department of Energy under Contract No. DE-AC05-84OR21400 with Martin Marietta Energy Systems, Inc. One of us (R.G) wishes to thank the Solid State Division at

Oak Ridge National Laboratory for its kind hospitality.

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