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Protons in neutron-irradiated and thermochemically reduced MgO crystals doped with lithium impurities

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H^- (hydride) ions have been observed in lithium-doped MgO crystals which have been neutron irradiated or thermochemically reduced (TCR). Infrared-absorption measurements have been used to identify the local modes of the H^- ions in these crystals. The concentration of the H^- ions in the neutron-irradiated crystals is found to be far less than that found in the TCR crystals. The thermal stability of H^- and oxygen vacancies in both oxidizing and reducing atmospheres are investigated. The emergence of sharp structures due to OH^- ions is attributed to the displacements of substitutional Li^+ ions, leaving behind unperturbed OH^- ions, via a mechanism of rapid radiation-induced diffusion during irradiation in a reactor. Results of neutron-irradiated MgO:Li, which had previously been oxidized at high temperature, are also presented.

I. INTRODUCTION

Hydrogen is an impurity that can affect the optical and electronic properties of many oxide crystals.[1-4] This is particularly true in lithium-doped MgO crystals (MgO:Li), because the presence of lithium ions induces an increased affinity and solubility for protons.[5,6] In the as-grown state MgO:Li crystals exhibit a very broad infrared band centered at 3430 cm^{-1} (0.425 eV), which is found only in MgO doped with lithium.[5] The full width at half maximum (FWHM) of this band is 190 cm^{-1} (0.24 eV) compared typically to 10 cm^{-1} associated with most OH^- ions, or OH^- complexes.[5]

The present work is divided into three sections. The first section concerns thermochemical reduction (TCR) of MgO:Li. The second and third sections address neutron-irradiated crystals of MgO:Li and MgO:Li which had previously been oxidized at high temperatures, respectively.

Thermochemical reduction, which is a very strong reduction process, involves heating a sample in a high-pressure vapor of the cation metal at high temperatures. This process leads to a stoichiometric deficiency of oxygen ions, resulting in oxygen vacancies. These vacancies are usually occupied by two electrons (F center) and are therefore electrically neutral.[7,8] At high temperatures protons can be trapped by these vacancies, forming H^- ions.[7-10] (The H^- ion is an oxygen vacancy occupied by a proton and two electrons and is therefore positively charged.) Hence TCR produces not only absorptions due to electronic transitions from oxygen vacancies but also vibrational modes of H^- ions. The first section reports the identification and thermal stability of H^- ions in MgO:Li before and after TCR.

We believe that it should be possible, in principle, to form H^- ions in a reactor that produces both neutron and γ rays. The neutrons produce oxygen vacancies by virtue of elastic collisions with the oxygen ions. The γ rays give rise to Compton electrons. These ionizing electrons displace protons from the defect configuration[5] responsible for the optical absorption band at 3430 cm^{-1}. This process—termed radiation-induced diffusion (RID)[11]—occurs with a phenomenally large cross section, thus rendering the protons highly mobile. In the second segment we show that indeed H^- ions in MgO:Li are formed in a fission reactor. In addition, we demonstrate that another light impurity ion, namely, Li^+, can also be displaced by RID. The relative cross sections for H^+ and Li^+ displacements are obtained.

Finally, in the third part we present results of neutron-irradiated MgO:Li crystals which had previously been oxidized at high temperatures.

II. EXPERIMENTAL PROCEDURES

Single crystals of MgO:Li were grown at the Oak Ridge National Laboratory by a variation of the carbon-arc fusion technique.[12] The starting material was high-purity MgO powder from the Kanto Chemical Company, Tokyo, Japan. Lithium doping was achieved by mixing 5% of Li_2CO_3 powder with MgO powder before crystal growth. The actual lithium concentration in the resulting single crystals was determined by spectrographic analysis to be 400 ppm.

As-grown MgO:Li crystals were thermochemically reduced in a tantalum chamber containing high pressure of magnesium vapor by heating at 1900 K and then fast cooled. Neutron irradiations were performed at the Oak Ridge National Laboratory Low Temperature Neutron Irradiation Facility up to a dose of 2×10^{17} n/cm^2 using a flux of 2.0×10^{13} fission-spectrum $n/cm^2\,s$ ($E>0.1$ MeV). During irradiation, the samples were cooled by flowing helium gas and the ambient temperature was about 320 K.

Optical measurements in the far infrared were made with a Perkin-Elmer 983G Infrared spectrophotometer. Measurements in the near-infrared, visible, and ultraviolet regions were made with a Perkin-Elmer Lambda 9 Spectrophotometer. Heat treatments were made either in flowing oxygen or inside a graphite container inserted in a horizontal furnace with flowing oxygen-free nitrogen gas.

III. RESULTS AND DISCUSSION

A. Thermochemically reduced crystals

In this section we shall incorporate results of undoped MgO crystals (TCR), some of which were performed in previous work, and compare them with the present work on MgO:Li.

1. H^- vibrational modes

Figure 1(a) depicts the infrared spectrum showing three H^- local modes at 1024, 1032, and 1053 cm^{-1} in a TCR undoped MgO crystal. For comparison, the spectrum for a MgO:Li crystal after TCR is shown in Fig. 1(b). While the intensity of the 1024-cm^{-1} band was comparable to that shown in Fig. 1(a), the 1032- and 1053-cm^{-1} bands were either largely or totally suppressed. The fact that the fundamental H^- ion vibrations with three sharp, closely spaced bands (none intensity correlated) were observed indicates that they are of different species, presumably with different impurity compensators.[8,13] It is apparent that the presence of lithium inhibits the formation of the H^- species responsible for these two bands. The H^- concentration in the MgO:Li crystal after TCR was estimated[8] to be 7×10^{17} cm^{-3}, a fraction of that obtained in a TCR undoped crystal.

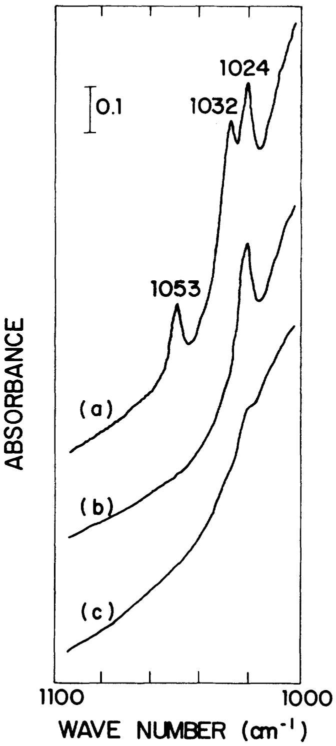

FIG. 1. Infrared absorption spectra for H^- ions: (a) cloudy MgO crystals with high hydrogen content, (b) Li-doped MgO after TCR, and (c) Li-doped MgO after neutron irradiation. The thicknesses of the samples are 0.3, 0.6, and 0.9 mm, respectively.

2. Thermal stability of H^- ions and anion vacancies

We performed annealing studies of TCR MgO and MgO:Li crystals in an oxidizing atmosphere. The results are plotted in Fig. 2. Three observations are noted. First, H^- ions in undoped MgO (curve a) are more stable than anion vacancies (curve c) when heated in oxygen. The same trend was obtained previously when similar crystals were heated in a reducing atmosphere.[8] This indicates that the presence of a proton in an oxygen vacancy stabilizes the vacancy against thermal annihilation. Second, all three H^- bands in undoped MgO crystals decrease at the same rate (Fig. 3). Third, H^- ions were much less stable in MgO:Li than in undoped MgO. This last observation is consistent with the results of previous experiments which showed that protons (or deuterons) are much more diffusive when Li impurities are present:[6] Deuterons diffuse into MgO:Li at temperatures as low as 800 K, whereas they do not in-diffuse in undoped MgO below 1750 K.

B. Neutron-irradiated MgO:Li

Two types of lithium-doped MgO crystals were neutron irradiated: as-grown crystals, labeled MgO:Li; and crystals oxidized at high temperatures, labeled MgO:Li(O). All neutron-irradiated crystals were aged for several years at room temperature. The present section addresses the first type, MgO:Li. The results of the second type, MgO:Li(O), will be presented and discussed in Sec. III C.

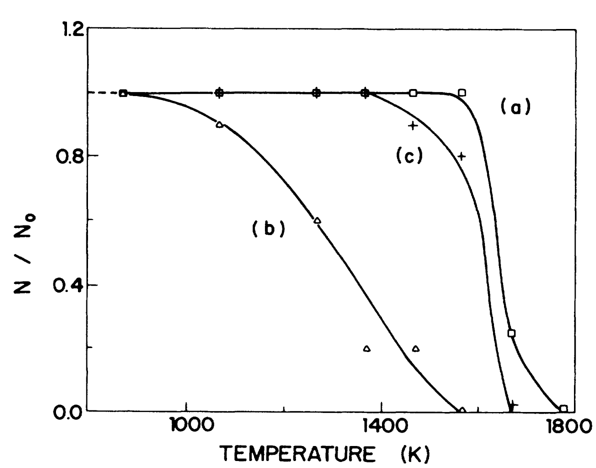

FIG. 2. Normalized concentration vs isochronal annealing temperature in flowing O_2 of (a) H^- ions in MgO, (b) H^- ions in MgO:Li, and (c) anion vacancies in MgO.

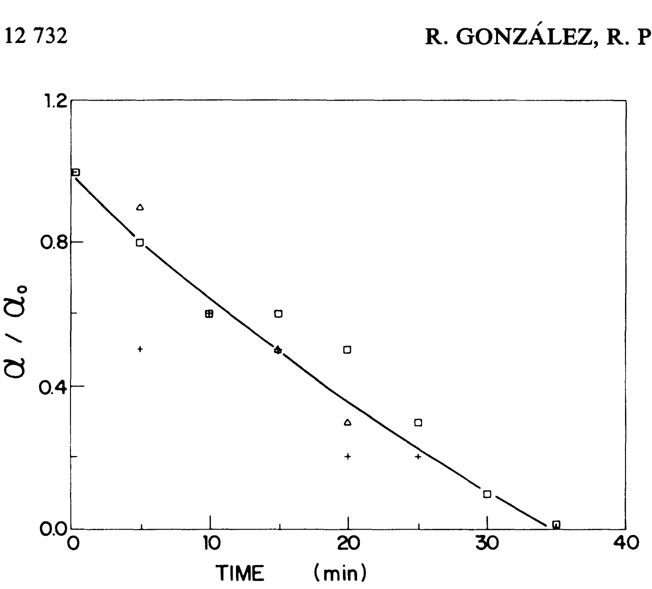

FIG. 3. Normalized absorption coefficient of H^- lines (Δ 1053 cm^{-1}, □ 1032 cm^{-1}, and + 1024 cm^{-1}) in MgO vs time after isothermal annealing at 1625 K in flowing O_2.

1. MgO:Li—the detection of H^- *ions*

After neutron irradiation of MgO:Li crystals, several changes were observed in the infrared spectra. Most significant was that as a result of the irradiation, there was a small band at about 1024 cm^{-1} [Fig. 1(c)], corresponding to a concentration of 0.8×10^{17} cm^{-3}. Even though this is a relatively small concentration, it nevertheless substantiates the principle of rapid proton diffusion under ionizing radiation established earlier.[11]

The confirmation of the existence of H^- signals in neutron-irradiated crystals leads to a fascinating question. Years ago it was observed that the presence of lithium impurities suppresses radiation damage in MgO.[14] Among the defects suppressed was anion vacancies.[14] Is it possible that in MgO:Li there was actually no suppression of anion-vacancy formation, but that the rest of the anion vacancies somehow had captured protons and were camouflaged as H^- ions? We shall quantitatively analyze the results: The concentration of anion vacancies, as obtained from the absorption coefficient of the 250-nm (5.0 eV), was 3.7×10^{17} cm^{-3}. This concentration is one-third of that found in an undoped crystal for the same neutron dose.[15] If this hypothesis is correct, then the H^- concentration needs to be about 8×10^{17} cm^{-3}. Our measurements showed that the H^- concentration was only 8×10^{16} cm^{-3}, or approximately 10% of the needed value. We therefore conclude that the presence of H^- ions was not in sufficient concentration to have camouflaged the loss of anion vacancies. There is no reason to believe that the suppression of radiation damage by lithium doping is not real.

2. MgO:Li—OH^- *absorptions*

Another notable change incurred by neutron irradiation is in the OH^- absorption region. The irradiation produced a decrease in the broadband absorption at 3430 cm^{-1}, and the emergence of sharp bands at 3370, 3345, 3320, and 3296 cm^{-1} (Fig. 4). These sharp bands are known to be present to a greater or less extent in virtually all other as-grown MgO crystals.[16] The most common band is that at 3296 cm^{-1}. It originates from the defect with the linear configuration: OH^--[++]-O^{2-} where [++] refers to a Mg^{2+} vacancy.[16] This defect is commonly referred to as the V_{OH}^- center.

We propose that the broad-absorption band at 3430 cm^{-1} is due to OH^- complexes associated with Li^+ impurities, since this band is observed only in Li-doped crystals. The sharp bands are due to OH^- vibrations not associated with lithium impurities.

3. MgO:Li—postirradiation annealing

We followed the thermal annealing behavior of the anion vacancies, H^-, and OH^- ions for two neutron-irradiated MgO:Li crystals. One was isochronally annealed for 15 min up to 873 K in a graphite crucible surrounded by flowing nitrogen. The other was annealed in oxygen. The heat treatments yielded essentially the same results. As noted above, the concentration of the anion vacancies was only one-third of that found in an undoped MgO for the same neutron dose. After annealing at 573 K, it decreased to 0.6 of its initial value. It completely vanished upon annealing at 873 K.

The H^- signal at 1024 cm^{-1} was stable up to 600 K. Annealing at temperatures above 650 K completely eliminates this band. Thus H^- ions in neutron-irradiated crystals are much less stable than in TCR crystals. This result is not surprising because of the existence of metastable oxygen interstitials in neutron-irradiated crystals. In the case of TCR crystals there are no interstitials to

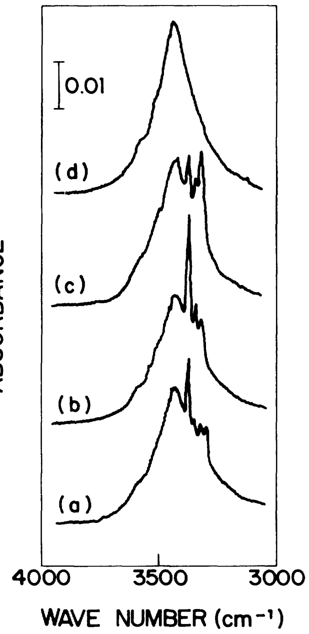

FIG. 4. Infrared absorption spectra of an as-grown MgO:Li crystal: (a) after neutron irradiation, and annealed at (b) 573 K, (c) 773 K, and (d) 873 K.

recombine with the vacancies; therefore the vacancies are thermally much more stable. The value of 600 K is consistent with the temperature at which oxygen interstitials recombine with oxygen vacancies in undoped irradiated MgO.[15]

The OH^- absorption spectra after neutron irradiation and subsequently isochronal annealed in oxygen is shown in Fig. 4. After neutron irradiation, several sharp bands were superimposed on the broad absorption at 3430 cm^{-1}. After annealing at 573 K, the 3370-cm^{-1} band reached its maximum intensity, whereas the 3296-cm^{-1} band was suppressed. The intensity of the 3320-cm^{-1} band increased at the expense of the 3370-cm^{-1} band during the anneal at 773 K. After the final anneal at 873 K, all the structures essentially vanished, and the broad absorption at 3430 cm^{-1} recovered to its initial value.

We propose that the emergence of the sharp bands at 3370, 3345, 3320, and 3296 cm^{-1}, which are superimposed on the 3430-cm^{-1}, is due to substitutional Li^+ ions having been displaced by the ionizing irradiation, leaving behind OH^- vibrational modes not associated with lithium ions. This would imply that the increase in absorption of the sharp bands occurs at the expense of the 3430-cm^{-1} band. The displacement of the Li^+ ions must necessarily be highly efficient. Indeed, it has been reported that Li^+ ions also experience RID similar to that observed for protons, but with a smaller cross section.[11] In the present case, the displacement mechanism of the Li^+ ion is similar to that of the protons and is caused by the γ rays in the reactor.

4. *MgO:Li—Li^+ displacement cross section*

Assuming that the sharp OH^- bands are produced by RID of Li^+ ions, we estimate the cross section for the displacement and compare it with the value reported previously.[17] The cross section for the displacement of an ion is given by $\sigma=(\Delta N/N)(1/\Delta\phi)$, where N is the initial concentration, ΔN the change in concentration, and $\Delta\phi$ the incremental dose. For protons the equation becomes $\sigma_p=(\Delta N_p/N_p)(1/\Delta\phi)$, and for Li^+ ions, it is $\sigma_{\mathrm{Li}}=(\Delta N_{\mathrm{Li}}/N_{\mathrm{Li}})(1/\Delta\phi)$. In the same crystal for a given dose, the two equations give the ratio

$$\sigma_p/\sigma_{\mathrm{Li}}=(\Delta N_p N_{\mathrm{Li}})/(N_p \Delta N_{\mathrm{Li}}) .$$

For our crystal, the initial concentration N_p is deduced from Eq. (A1) to be 3×10^{17} cm^{-3} (see Appendix). We now proceed to determine ΔN_p and ΔN_{Li} experimentally. The amount of displaced protons is of the order of the observed hydride concentration, 0.8×10^{17} cm^{-3}. The amount of displaced lithium ions can be estimated assuming that for each displaced Li^+ ion one OH^- radical (unperturbed by a Li^+ ion), such as the V_{OH}^- defect, is created. According to Eq. (A1) this concentration is estimated to be 0.2×10^{17} cm^{-3}. These values give a $\sigma_p/\sigma_{\mathrm{Li}}$ ratio of 2.5×10^2. The cross section σ_p is known to be 10^8 b (where 1 b = 10^{-24} cm^2). Therefore σ_{Li} becomes 4×10^5 b. This value is consistent with a previous finding which uses an entirely different approach.[17]

C. Neutron-irradiated MgO:Li(O)

This section concerns MgO:Li(O), or lithium-doped MgO which had previously been oxidized at high temperatures. After oxidation for 3 h at 1600 K, the samples exhibit the characteristic blue coloration due to $[Li]^0$ defect which absorb light at 690 nm (1.8 eV) (Ref. 18) [see Fig. 5(a)]. This defect is a substitutional Li^+ ion adjacent to an O^- ion, and has the linear configuration: O^{2-}-Li^+-O^-.

1. *MgO:Li(O)—$[Li]^0$ defects and H^- ions*

After the oxidation the absorption of the 3430-cm^{-1} band decreased dramatically, consistent with a previous report.[19] The decrease could be due to either a relocation of protons to sites not infrared active, or to outdiffusion of protons. In order to determine which process prevails, an as-grown MgO:Li sample was first deuterated by heating in D_2O vapor for 3 h at 1273 K. The 2550-cm^{-1} OD^- analog of the 3430-cm^{-1} band was observed. Subsequently this sample was oxidized for 2 h at 1523 K. After the oxidation the OD^- band vanished. Following an anneal at 1073 K in a graphite crucible with flowing nitrogen, the OH^- signal at 3430 cm^{-1} increased, but no OD^- absorption was observed. These results showed unambiguously that during oxidation protons or deuterons are effectively driven out of the crystal. Presumably the subsequent anneal at 1073 K reintroduced protons either from the high-pressure cavities[20] in the crystal or from the atmosphere.

After neutron irradiation of MgO:Li(O) crystals, three observations were noted. First, no H^- ions were observed. This result is not unexpected, since we have already shown that the proton concentration was drastically reduced during oxidation. Second, a very large decrease in the 1.8-eV absorption was observed [Fig. 5(b)], consistent with a previous report.[18] The holes from the $[Li]^0$ defect presumably recombined with electrons from multivacancies created by the neutron bombardment.[5] Third, there were no structures superimposed on the 3430-cm^{-1} band, in marked contrast with MgO:Li crystals. The reason is that oxidation of MgO:Li crystals has

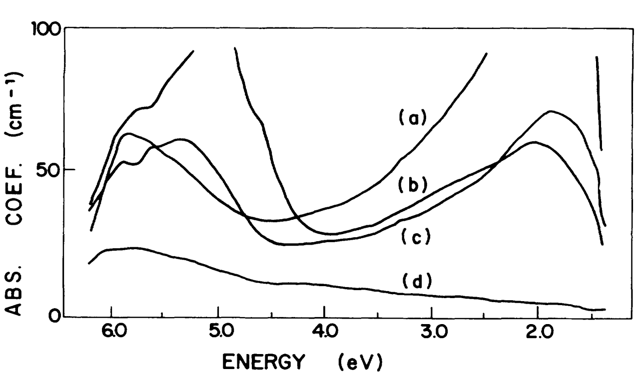

FIG. 5. Optical absorption spectra of a MgO:Li crystal: (a) oxidized at 1600 K, (b) oxidized at 1600 K followed by neutron irradiation, and subsequently annealed at (c) 773 K and (d) 1073 K.

the net effect of dispersing Li^+ ions into the matrix from Li_2O precipitates,[21] in addition to losing protons, thus preventing the appearance of the superimposed structure. Hence, substitutional Li^+ ions in the matrix could increase by a factor of 10^2, and protons decrease by a factor of 10. Therefore the displacement of one Li^+ ion is unlikely to leave behind an OH^- ion unperturbed by other Li^+ ions.

2. *MgO:Li(O)—postirradiation annealing*

Two MgO:Li(O) samples were neutron irradiated. One was subsequently isochronal annealed in a graphite capsule for 15 min up to 1073 K, whereas the other was annealed in flowing oxygen. Both atmospheres yielded essentially the same results, although oxygen appeared to be slightly more effective in annealing out the anion vacancies. The results for the oxygen annealing are shown in Figs. 5(c) and 5(d). On the other hand, not surprisingly, heating in a reducing atmosphere annealed out the oxygen-generated 1.8-eV band a little faster. After the anneal at 773 K [Fig. 5(c)], the 5.0-eV band decreased appreciably and a significant increase is observed in the 1.8-eV band. We attribute the increase in the $[Li]^0$ to the release of holes from the annihilation of defects produced by neutron bombardment. The final anneal at 1073 K almost completely destroyed the 1.8-eV band [Fig. 5(d)]. This is consistent with a previous report that between 700 and 1300 K heating in any atmosphere would annihilate the $[Li]^0$ band;[22] the atmosphere determines the rate of annihilation.

Figure 6 shows the infrared spectra of the neutron-irradiated MgO:Li(O) crystal and after subsequent anneals in oxygen. As noted, the as-irradiated spectrum [Fig. 6(a)] exhibited a weak 3430-cm^{-1} band. After the anneal at 573 K, two intense sharp bands at 3370 and 3345 cm^{-1} appeared [Fig. 6(b)]. Successive anneals at increasing temperatures changed the relative intensities of these bands [Fig. 6(c)]. After the final anneal at 1073 K [Fig. 6(d)], the initial intensity of the 3430-cm^{-1} band before oxidation was restored.

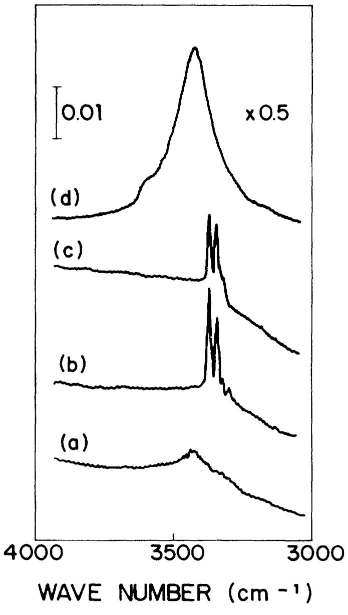

FIG. 6. Infrared absorption spectra of an oxidized MgO:Li crystal: (a) after neutron irradiation, and annealed at (b) 573 K, (c) 773 K, and (d) 1073 K.

IV. SUMMARY AND CONCLUSION

The present study focuses on protons in three types of lithium-doped MgO crystals: (1) thermochemically reduced (TCR), (2) neutron irradiated, and (3) neutron-irradiated crystals which had previously been oxidized at high temperatures.

TCR produces primarily anion vacancies and H^- ions.[7,8] Whereas three local modes are observed in undoped MgO crystals, only one of them (1024 cm^{-1}) is present in significant quantity in lithium-doped crystals. The bands at 1032 and 1503 cm^{-1} are suppressed by the presence of lithium. The hydride ions in MgO:Li are much less stable than those in undoped MgO. This observation is compatible with previous studies which show that protons are much more mobile when lithium impurities are present.[6]

Neutron irradiation of MgO:Li produces H^- ions, as well as anion vacancies. In principle, the production of H^- ions in a fission reactor is not unexpected, because of the preponderance of neutrons and gamma rays. The neutrons produce oxygen vacancies and the γ rays provide Compton electrons which displace protons from V_{OH}^- with a phenomenally large cross section—a process termed radiation-induced diffusion.[11] These H^- ions anneal between 600 and 650 K and are therefore much less stable than those produced by TCR. Unlike TCR crystals, neutron-irradiated crystals contain metastable oxygen interstitials which can recombine with the oxygen vacancies at relatively lower temperatures.

The existence of H^- ions raises a pertinent question regarding the issue of the suppression of radiation damage in MgO by lithium doping. Is it possible that in MgO:Li there was actually no suppression of anion vacancy formation, but that anion vacancies somehow capture protons and are camouflaged as H^- ions? A quantitative analysis was carried out. We conclude that H^- ions are not in sufficient quantity to have camouflaged the loss of anion vacancies.

Changes are also observed in the OH^- regime. Prior to irradiation, only a broadband absorption at 3430 cm^{-1} is observed. This band is attributed to OH^- complexes associated with lithium, because this band is observed only in lithium-doped MgO. After the irradiation, sharp bands are observed to be superimposed on the broadband. These sharp bands are observed in crystals which do not contain lithium, and are therefore attributed to OH^- ions not associated with lithium impurities. We attribute the emergence of the sharp bands to the displacements of Li^+ ions by the highly efficient mechanism of radiation-induced diffusion,[11] leaving behind OH^- ions unassociated with lithium. Using experimental values in the present study, we obtained an estimate for the displacement cross section of lithium and found that it is consistent with a previous study which uses an entirely different approach.[17]

In contrast, neutron irradiation of MgO:Li which previously underwent oxidation at high temperature produced no H^- ions and no structures superimposed on the drastically reduced 3430-cm^{-1} band. The cause is attributed to a loss of protons during oxidation, a fact established in an experiment using deuterons. During oxidation, lithium ions diffuse into the matrix from Li_2O precipitates and becomes substitutional ions, in addition to the loss of protons. Therefore the displacement of one substitutional lithium ion during irradiation is much less likely to leave behind an OH^- ion unperturbed by other Li^+ ions.

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APPENDIX

The initial hydrogen concentration responsible for the 3430-cm^{-1} band can be estimated using a modification of Smakula's dispersion theory.[23,24] The outcome of the calculation is that

$$N(OH^-)=1.2\times 10^{19}\mu\,\Delta E\ \text{cm}^{-3}\ , \qquad \text{(A1)}$$

where $N(OH^-)$ is the OH^- concentration per cm^3, μ is the absorption coefficient, and ΔE is the FWHM in electron volts.

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