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# Oxidation and reduction of lithium-containing MgO at high temperatures

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The effect of oxidation and reduction on Li-containing MgO crystals at temperatures up to 1600 K is reported. Heating in oxidizing atmospheres followed by fast cooling produces stable $[\mathrm{Li}]^0$ defects, whereas similar treatment in a reducing atmosphere does not. Annealing rates of these defects also depend on whether the crystals are in an oxidizing or reducing atmosphere. A short-range diffusion mechanism is proposed to describe the atmospheric dependence of $[\mathrm{Li}]^0$-defect production. Heating to ~ 1500°K, regardless of the ambient atmosphere, gives rise to a broad optical absorption band at ~ 5.3 eV, which we believe to be associated with lithium. Optical excitation of this band produces a luminescence which peaks near 2.7 eV.

## I. INTRODUCTION

Under the conditions of high temperatures and oxidizing atmospheres prevalent in magnetohydrodynamic applications, polycrystalline magnesia is exposed to streams of alkali ions. The presence of alkali-metal impurity ions imbedded in the magnesia can result in changes in its thermal and electrical properties. Alkali ions in MgO usually cannot be detected by spectroscopic techniques because they are neither optically absorbing nor paramagnetic. However, substitutional alkali ions can be detected if a hole is trapped at a neighboring anion site. The properties of such trapped-hole defects in single-crystal alkaline-earth oxides have been studied.[1-9] The alkali ions are introduced either by diffusion or during crystal growth and can subsequently be identified at cation sites through the optical and paramagnetic properties of the hole trapped at a neighboring $O^{2-}$ ion due to ionizing radiation at low temperatures. The hole and the alkali ion form the electrically neutral $[\mathrm{alkali}]^0$ defect. The trapped hole normally begins to leak off the neutral defect[3] at ~200 K and finds itself contributing to valence changes of metallic impurity ions.

In the case of lithium-doped MgO crystals, not only can the $[\mathrm{Li}]^0$ defects be formed at low temperatures by ionizing radiation, but it was discovered that heat treatment at high temperatures in air can create the same $[\mathrm{Li}]^0$ defects in a form which is stable well above room temperature.[10] Furthermore, the concentration of $[\mathrm{Li}]^0$ defects that can be thermally generated exceeds that which can be created by ionizing radiation at low temperatures.

In order to explain the vastly contrasting stability of these spectroscopically identical defects, it was proposed that the source of the defects is different.[11] According to this model, the $[\mathrm{Li}]^0$ defects that cannot survive room temperature are due to $\mathrm{Li}^+$ ions, which are randomly distributed throughout the crystal in soluble substitutional form and are charge compensated by impurities such as $\mathrm{Fe}^{3+}$, $\mathrm{Cr}^{3+}$, and $\mathrm{Mn}^{4+}$. The thermally generated defects, on the other hand, originate from lithium-rich precipitates which at high temperatures give rise to "microgalaxies" containing high concentrations of substitutional lithium ions. Charge neutrality within each microgalaxy would assure that the lithium ions be in the neutral state—the $[\mathrm{Li}]^0$ defects.

Transmission-electron-microscope (TEM) investigations of as-grown Li-doped MgO have indeed revealed the presence of precipitates.[12] Microdiffraction studies and Moiré-pattern analysis have identified these precipitates as $\mathrm{Li_2O}$ with the cubic fluorite structure. Heating the crystal at high temperatures in air followed by fast cooling leads to a reduction of precipitate size. These results confirm that diffusion of lithium ions from precipitates is involved.

In this paper we describe our efforts to gain some insight into the ionic processes involved in the thermal generation and annihilation of the stable $[\mathrm{Li}]^0$ defects in MgO. Specifically, we found that the concentration of this defect is strongly dependent on the atmosphere in which the crystal is heated. The presence of oxygen in the atmosphere has been demonstrated to be a requisite for the thermal generation of these defects.

## II. EXPERIMENTAL PROCEDURE

The crystals used in this work were grown by an arc-fusion technique[13] using high-purity MgO powder from the Kanto Chemical Co. (Tokyo). The starting powder was mixed with reagent-grade $\mathrm{Li_2CO_3}$ powder to a concentration of about 5% by weight, but the actual concentration of lithium in the resulting single crystals was determined by spectrographic analyses to be approximately 0.03 to 0.05 at.%.

A Sentry Model 7AV furnance with a 3.2-cm-*i* diam quartz tube inserted in the horizontal axial hole was used for heating the samples. The samples could be heated in static air (no air flowing), flowing oxygen, or flowing hydrogen atmospheres. When samples were to be heated in flowing hydrogen (99.999% pure), special care was taken to eliminate oxygen from the quartz tube by first passing nitrogen through it. The crystals were heated in a given atmosphere for 10 min at each of several different temperatures. Following each 10 min period, the samples were pulled quickly out of the furnace portion of the tube to the room temperature portion of the tube (still in their respective atmospheres). The process of heating the sample followed by pulling the sample out quickly constituted the freezing in of defects generated by the heat treatment.

Optical absorption measurements were taken on a Cary Model 14R spectrophotometer at room temperature. For the low-temperature photoemission studies, a Sulfrian optical cryostat was used. A 200-W high-pressure Hg lamp mounted on a Bausch and Lomb monochromator set at $\lambda = 245$ nm was used as an excitation source. The detection system consisted of a Jarrell-Ash scanning spectrometer in conjunction with an EMI 9658R photodetector cooled to −30°C. The wavelength response of the detection system was calibrated using a standard quartz-iodine lamp with a calibration derived from the National Bureau of Standards.[14]

## III. RESULTS AND DISCUSSION

### A. Optical spectra and production of stable $[\mathrm{Li}]^0$ defects

In order to minimize variations of Li or other impurity concentrations, the samples used were obtained from the same ingot. The samples were heated at various temperatures in static air, flowing oxygen, or flowing hydrogen for 10 min. and cooled rapidly. Flowing hydrogen assures the absence of oxygen in the atmosphere.

Figure 1 illustrates the optical absorption spectra of a crystal measured before and after each heat treatment in static air at increasing temperatures. The quartz tube inserted in the furnace was left open at both ends. The crystal was placed in the tube at the midpoint of the furnace, left for 10 min and pulled out quickly to the room-temperature portion of the tube for cooling. The dotted curve corresponds to the sample in the virgin or "as-grown" state before any heat treatment. The large absorption in the uv region ($\alpha \sim 20$ cm$^{-1}$) is characteristic of lithium-doped MgO. There also appears to be absorption corresponding to the 4.3-ev $\mathrm{Fe}^{3+}$ band. After heating the sample at 1296 K, a band at 1.8 eV, which has been unequivocally identified to be due to the $[\mathrm{Li}]^0$ defects,[9,10] emerges and the absorption in the uv diminishes. The latter is due in part to the diminished intensity of the 5.7-eV $\mathrm{Fe}^{3+}$ band caused by the change in valence of the $\mathrm{Fe}^{3+}$ during the heat treatment, a fact which has been verified by EPR studies.[15] Heat treatments at still higher temperature yield large absorptions at 1.8 eV and in the 5–6-eV region.

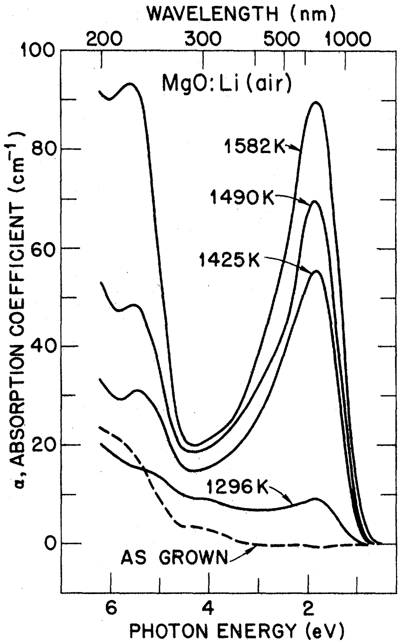

FIG. 1. Optical-absorption spectra of a Li-doped MgO crystal heated at different temperatures in static-air (without flowing air). Measurements were made at room temperature.

Figure 2 shows the differential spectra, which were taken by subtracting the absorption of the as-grown curve from each of those illustrated in Fig. 1. In effect, the spectra in Fig. 2 may be considered to correspond to the net absorption due to thermal treatments in static air. What appears to be a broad band at ~5.5 eV in Fig. 1 is really a band at ~5.3 eV in Fig. 2, due to negation of the strong uv absorption of the as-grown spectrum. The defect responsible for this absorption appears to be diamagnetic and has not been identified. However, since this band has not been observed in lithium-free crystals, it is believed to be associated with lithium. Another band of low absorption coefficient was observed at 2.7 eV. It did not emerge with thermal treatment until $[\mathrm{Li}]^0$ defects appeared.

Figure 3 displays the differential optical absorp-

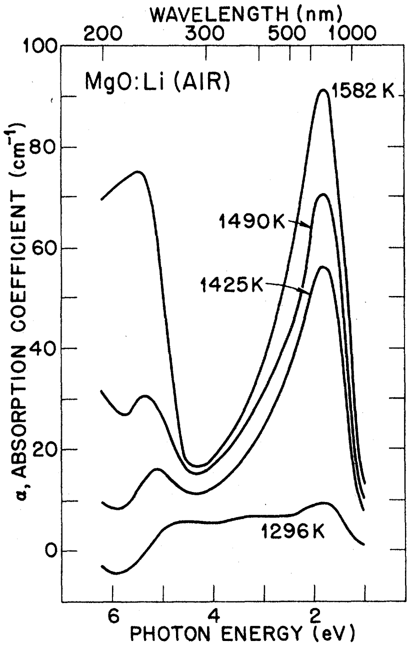

FIG. 2. Differential optical absorption spectra, taken by subtracting the absorption of the "as-grown" curve from each of those illustrated in Fig. 1, due to heat treatment at different temperatures in static air.

tion spectra of a sample after each heat treatment in a flowing oxygen atmosphere at increasing temperatures. The same procedure was followed as with the air except that oxygen was blown into the tube from one end while the other end had a tube leading from it to an exhaust. When the sample was pulled, it was allowed to cool in the oxygen atmosphere at the room-temperature portion of the tube. Again the primary absorption bands were at 5.3 and 1.8 eV. Compared with the corresponding spectra obtained for static air (Fig. 2), the absorption coefficients of the 1.8-eV band were much larger, while those of the 5.3-eV band were comparable. It should be noted that no 5.0-band attributed to anion vacancies[16] was detected in Figs. 1–3, confirming a previous work.[11]

The differential absorption spectra of a crystal after heating in a hydrogen atmosphere at different temperatures are illustrated in Fig. 4. These spectra are characterized by the complete absence of the 1.8-eV band and the growth in intensity of the 5.3-eV band with temperature. A comparison of the 5.3-eV bands obtained from crystals which were heated in static air, oxygen, or hydrogen at a given temperature yielded no major difference in their absorption coefficients; i.e. for thermal treatment at $T\sim 1600$ K, the absorption coefficients of the 5.3-eV band in all three cases were in the neighborhood of ~100 cm$^{-1}$. In order to verify that the complete absence of [Li]$^0$ defects was due to the lack of oxygen in the atmosphere rather than the presence of hydrogen, four other samples were heated in other reducing or inert atmospheres: one in CO gas at 1600 K; one in ox-

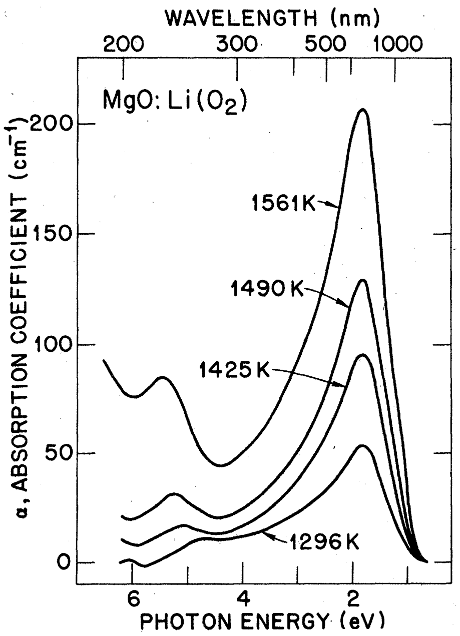

FIG. 3. Differential optical absorption spectra of a crystal heated at different temperatures in flowing oxygen.

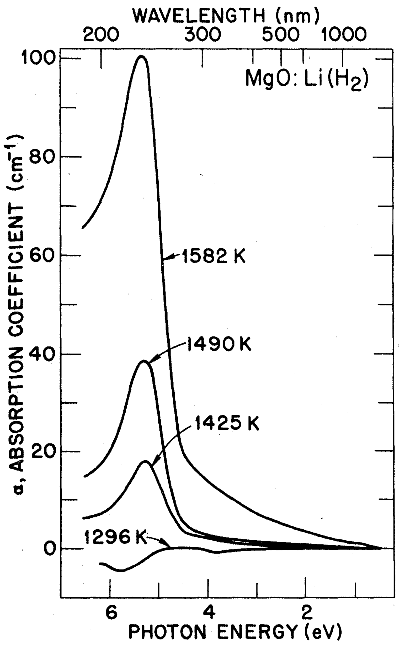

FIG. 4. Differential optical absorption spectra of a crystal heated at different temperatures in flowing hydrogen.

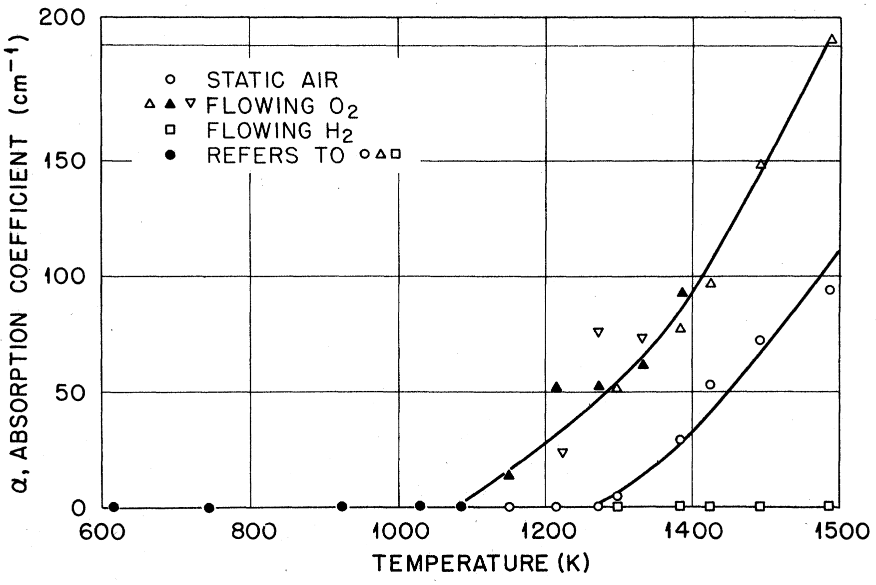

FIG. 5. Absorption coefficient of the 1.8-eV band as a function of air, oxygen, and hydrogen. △, ▲ and ▽ refer to three different crystals heat-treated in flowing oxygen (the latter two are adjacent crystals).

ygen-free $N_2$ gas at 1600 K; one in argon gas at 1500 K, and one in high-pressure Mg vapor at ~1900 K in an enclosed tantalum bomb. The results were the same: no $[\mathrm{Li}]^0$ defects.

In Fig. 5, the absorption coefficient of the 1.8-eV band is plotted as a function of temperature for all three crystals, using values obtained from the spectra shown in Figs. 2–4. In the case of heat treatment in static air, $[\mathrm{Li}]^0$ defects began to form at $T\sim 1300$ K, and the resulting growth curve was similar to the one obtained previously, which was also performed under static air conditions.[11] Heating in an oxygen atmosphere was more efficient for the generation of $[\mathrm{Li}]^0$ defects than heating in static air. Indeed the threshold temperature was appreciably lower at $T\sim 1100$ K. Several sets of adjacent samples were used which confirmed the difference in threshold temperature, even though there were some minor variations between different sets of samples. The onset of color with increasing temperature could be discerned at the same edge of the adjacent samples by the naked eye even before it could be detected in the bulk. The optical-absorption values in the figures represent the bulk absorption. It should be noted that heating in a sample with flowing air yields a growth curve which nearly coincides with that for flowing oxygen.

The thermally generated 5.3-eV absorption band which we believe to be associated with lithium gives rise to a luminescence when excited optically. Figure 6 illustrates the emission spectra for the crystal which had been heated in hydrogen at 1582 K and whose absorption spectrum is shown in Fig. 4. Crystals which exhibit the 1.8-eV band, such as those heated in air or oxygen, are not useful for emission studies due to self absorption of the luminescence. Two rather unusual observations are made from the temperature dependence of the luminescence spectra, induced by the 245-nm Hg exciting light. One is that the half-width is higher at low temperatures, being 0.85 eV at 112 K and 1.0 eV at 7 K. The

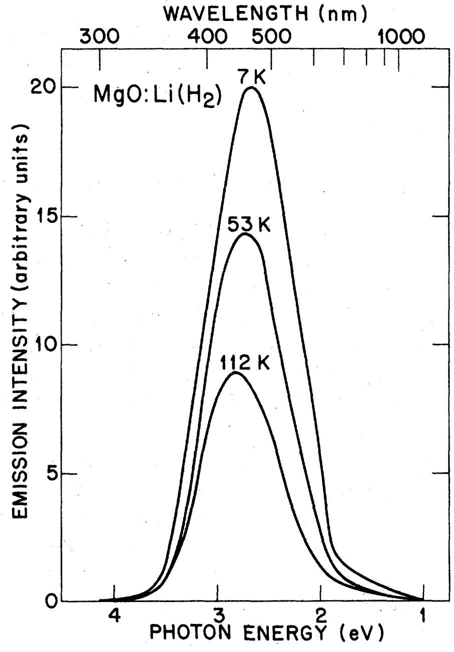

FIG. 6. Luminescence spectra due to optical excitation of the 5.3-eV absorption band in a crystal previously heated in hydrogen atmosphere at 1582 K.

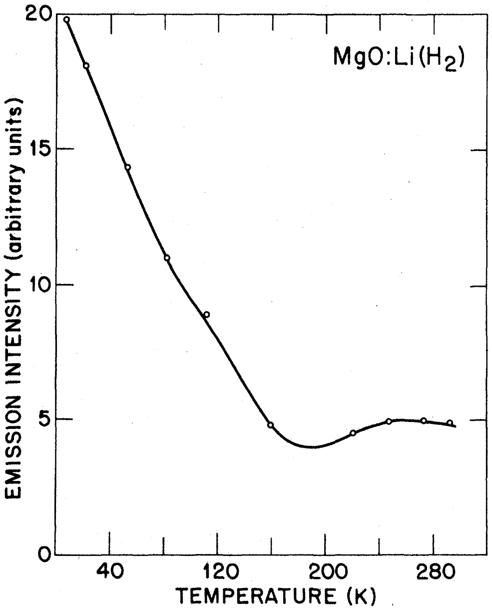

FIG. 7. Temperature dependence of the luminescence intensity resulting from 254-nm optical excitation of the 5.3eV absorption band in a crystal previously heated in hydrogen atmosphere at 1582 K.

other observation is that as the temperature decreases, the emission-band peak shifts toward lower energy, from ~2.8 to ~2.6 eV. It appears, therefore, that two or more overlapping emission bands are involved, with a lower energy band prevailing at low temperatures. The temperature dependence of the emission intensity up to room temperature is plotted in Fig. 7. Below $T \sim 200$ K, the emission intensity, as monitored at 2.7 eV, decreases with rising temperature.

### B. Production of unstable $[\mathrm{Li}]^0$ defects by optical bleaching

$[\mathrm{Li}]^0$ defects which are unstable at room temperature can be created at 77 K by optical bleaching of crystals quenched from high temperatures and containing stable $[\mathrm{Li}]^0$ defects. This is shown in Fig. 8. A sample was heated in an oxygen atmosphere at 1157 K and cooled rapidly, resulting in $\alpha_0 \sim 12$ cm$^{-1}$ for the 1.8-eV band. Maintained at 77 K in an optical cryostat, the sample was irradiated with light either from a 200-W high-pressure Hg source passing through a monochromator or from a He-Ne laser. Initially the sample in the cryostat was irradiated with 5.07-eV (245-nm) light. A 35-min excitation was performed, with two intervening optical absorption measurements to assure that saturation of the $[\mathrm{Li}]^0$ concentration at $\alpha/\alpha_0 \sim 1.46$ had been attained. However, upon warming the crystal to room temperature, the absorption coefficient reverted back to $\alpha_0$, indicating that the $[\mathrm{Li}]^0$ defects created by the optical bleaching were unstable at room temperature. These defects are attributed to substitutional $\mathrm{Li}^+$ ions soluble in the MgO matrix. The sample was then cooled again and the optical bleaching repeated for additional 35-min periods using light of another wavelength corresponding to the other major Hg lines, and the 632.8-nm light of a 0.5-mW He-Ne laser. It is observed from the figure that high-energy photons are capable of producing more $[\mathrm{Li}]^0$ defects than low-energy photons. Holes from the higher energy bands are apparently more readily released and trapped at $\mathrm{O}^{2-}$ sites next to substitutional $\mathrm{Li}^+$ ions.

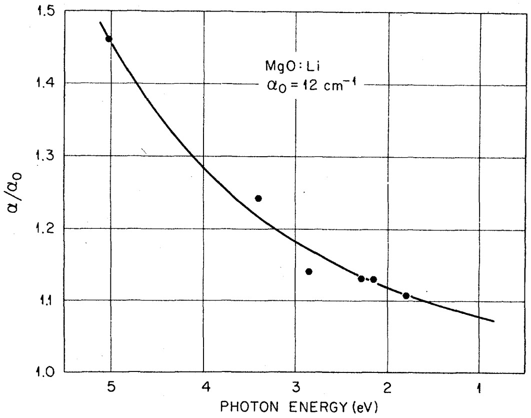

FIG. 8. Increase in the absorption coefficient of the 1.8-eV band due to optical bleaching at 77 K with photons of differenct wavelengths.

### C. Thermal annihilation

$[\mathrm{Li}]^0$ defects thermally generated can also be thermally annealed out. In this series, four samples of comparable thickness, ~0.9 cm, were used. The preanneal sample preparation involved heating the four crystals at 1306 K for 10 min in a flowing oxygen atmosphere and fast cooling. This procedure results in an $\alpha_0 \sim 60$ cm$^{-1}$ for the 1.8-eV absorption band. Each of the samples was isothermally heated up to 66 min in static air at a given temperature ranging from 566 to 1149 K. The normalized absorption coefficient $\alpha/\alpha_0$, is plotted as a function of time for all four samples in Fig. 9. Decay was expectedly most rapid at the higher temperatures. The extent of the decay after 3 min at each of the four temperatures is plotted as a function of the annealing temperature $T_A$ in the inset. Clearly $-\Delta\alpha/\alpha_0$ is larger at higher $T_A$.

Furthermore, not only is the temperature critical for annealing, but the ambient atmosphere also plays a fundamental role in the annihilation process. A sample was split into two pieces

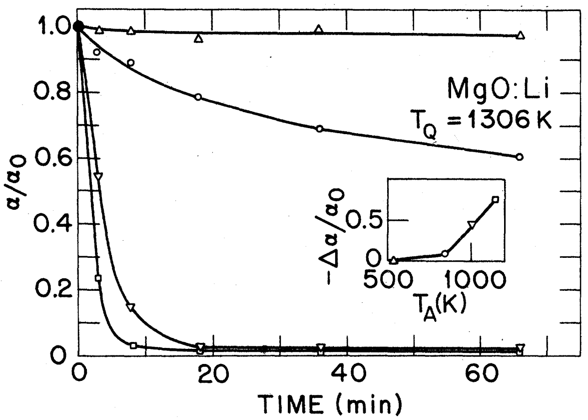

FIG. 9. Isothermal annealing of thermally generated [Li]$^0$ defects at $T$= 566, 855, 1009 and 1149 K (△, ○ ▽ and □, respectively).

along the narrow dimension. The twin samples were then heated at 1300 K in an oxygen atmosphere, resulting in an $\alpha_0$= 45 cm$^{-1}$ for the [Li]$^0$ band. Then both samples were isothermally annealed at 826 K, one in a flowing oxygen atmosphere and the other in a flowing hydrogen gas. The results are illustrated in Fig. 10. The annealing process of the [Li]$^0$ defects proceeds much more rapidly in a reducing atmosphere. For example, after 40 min in hydrogen no [Li]$^0$ defects can be detected, whereas in the case of annealing in oxygen about 30% of the defects still remain. To be sure, the reduction process was not uniform over the flat surface of the crystals. Reduction was initially more prominent at the edges and progressed towards the center of the samples in time.

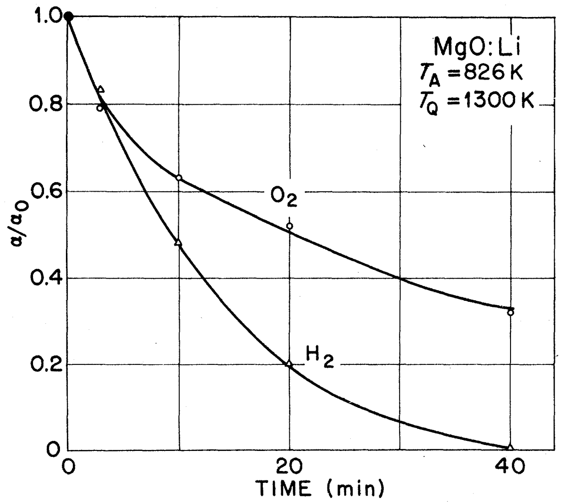

FIG. 10. Isothermal annealing of thermally generated [Li]$^0$ defects at 826 K in oxygen and hydrogen atmospheres.

## IV. SUMMARY AND CONCLUSION

The results of the present investigation on the high-temperature behavior of lithium-doped MgO can be summarized as follows:

(i) At elevated temperatures, the formation of stable [Li]$^0$ defects, monitored by the 1.8-eV band, is strongly dependent on the atmosphere in which the crystal is heated. The presence of oxygen in the atmosphere is a requisite for the thermal generation of these defects.

(ii) Thermal treatment gives rise to a broad absorption of ~5.3 eV whose absorption coefficient appears to be independent of the ambient atmosphere. Optical excitation into this band induces a luminescence which peaks at 2.6–2.8 eV.

(iii) The annihilation at a given temperature of thermally generated [Li]$^0$ defects also depends on the ambient atmosphere, being more rapid in a reducing gas.

In a previous study[12] employing electron diffraction and TEM techniques, it was established that $Li_2O$ precipitates are present in as-grown Li-doped MgO crystals and that as a result of heat treatment in static air, these precipitates diminish in size. The regions previously occupied by the lost $Li_2O$ were presumably replaced by MgO, since no hollow envelope around the precipitates was detected. These observations are compatible with an earlier proposal[11] that precipitates contribute to substitutional $Li^+$ ions in the MgO matrix. Effectively, for every two $Li^+$ ions leaving the $Li_2O$ precipitate due to thermal dissociation, only one $Mg^{2+}$ enters to form MgO. From stoichiometric considerations, the lack of oxygen ions (or excess of cations) in the crystal can result in the formation of oxygen vacancies or be offset by an external supply of oxygen. Since charged oxygen vacancies, which are optically absorbing at 5.0 eV, have not been observed in this study or in earlier work,[10,11,17] the requirement of a source of oxygen is compatible with the previously proposed model of thermal diffusion of $Li^+$ ions from $Li_2O$ precipitates to substitutional sites in the MgO matrix in order to explain stable [Li]$^0$ defects.

The experimental observation that the availability of oxygen at the crystal surface would have such a ready impact in the bulk of the crystal would seem at first to suggest long-range migration of oxygen ions. However, the diffusion coefficients of oxygen ions in MgO (Ref. 18) are too small in the 1300–1600-K range and would preclude the possibility of such a mechanism. The same can be argued for diffusion for magnesium ions.[19] We propose a mechanism involving short-range ionic migration to explain the apparent surface-to-bulk or dislocation-to-bulk transport phenomenon. At high temperatures the predominant intrinsic defects in MgO are of the Schottky type,[20] which are vacancies left behind when cations and anions are removed from the interior of the crystal added to the surface to form new layers of the crystal.[21] The requirement that the solute around each precipitate effectively exchanges one $Mg^{2+}$ ions for two $Li^+$ ions from the precipitate indicates that there exists an excess of cations in the MgO matrix. These cations can migrate short distances to recombine with Schottky defects in the cation sublattice. At a given temperature the concentration of Schottky defects is determined by the Boltzmann factor $\exp(-E/kT)$. Since excess cations would perturb this equilibrium concentration, new Schottky defects in the cation sublattice are formed to restore equilibrium, thereby providing $Mg^{2+}$ ions an opportunity to migrate to the sample surface or dislocations. If a source of oxygen is available at the surface, magnesium oxide monolayers will be formed, analogous to the formation of nonstoichiometric MgO in high-pressure Mg vapor at high temperatures (commonly called additive coloration). In the case of a reducing or inert atmosphere, space-charge considerations[15] would forbid the formation of microgalaxies.

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