

## Laser-induced-impurity colloid formation and dissociation in MgO single crystals

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Optical-absorption measurements were used to monitor impurity precipitation and dissociation of precipitates in both laser-irradiated and furnace-annealed MgO single crystals doped with Li, Co, or Ni impurities. In as-grown MgO:Li crystals, both Li<sub>2</sub>O precipitates and isolated substitutional Li<sup>+</sup> ions are present; oxidation above 1100 K disperses lithium ions from the precipitates and forms stable [Li]<sup>0</sup> centers (substitutional Li<sup>+</sup> ions, each with a trapped hole) around the precipitates. Laser-induced experiments showed that both lithium precipitation and dispersion were enhanced by the presence of cracks in the samples. A cross-section value of 0.2 bs was obtained for Li displacement, indicating that the diffusion of lithium occurs via a thermal process rather than a radiation-induced diffusion, as in the case of ionizing radiation. In MgO:Co crystals, metallic colloids were produced by thermochemical reduction at high temperatures that resulted in an extinction band at 3.7 eV due to Mie scattering from the precipitates. Dissociation of cobalt precipitates was produced under laser irradiation. An activation energy of 3.0 eV and a cross section of 0.01 b s was obtained for displacement of cobalt ions from the precipitates. Laser-induced desorption and ablation was observed when the laser was focused on the crystal. In nickel-doped MgO crystals, an activation energy of 1.9 eV was determined for displacement of Ni ions from the metallic nickel precipitates. In such crystals, different patterns can be inscribed with the laser. [S0163-1829(98)09533-2]

### I. INTRODUCTION

Many interesting phenomena can occur when light from a high-power laser is absorbed in the near-surface region of solids. In wide-band-gap insulators such as MgO, ion desorption and ablation has been reported in ultraviolet-irradiated (5 eV photons) crystals at fluences of 2–12 J/cm<sup>2</sup>, and these processes are enhanced by mechanically produced defects.<sup>1–6</sup> Laser annealing has been widely applied to anneal ion-implanted semiconductors and metals,<sup>7–13</sup> and to a much lesser extent to insulators where it has been used for studies of laser damage investigations.<sup>14–16</sup> Recently, colloids have been dissociated by pulsed laser annealing in ion-implanted sapphire, float glass, and silica.<sup>17–19</sup>

In general, thermochemical reduction (TCR) of oxide crystals at sufficiently high temperatures causes precipitation of metal substitutional impurities characterized by broad extinction bands attributed to Mie scattering from precipitates.<sup>20–28</sup> For cobalt and nickel impurities in reduced MgO, the maxima of the extinction bands are located at about 3.7 and 2.2 eV, respectively.<sup>21,24</sup> In these crystals, the concentration of metallic colloids can be monitored by the growth rate of the corresponding extinction bands at 3.7 and 2.2 eV.<sup>21,24</sup> Subsequent thermal anneals at temperatures higher than ~1300 K in an oxidizing atmosphere disperse the ion impurities from the precipitates, which first decrease in size and eventually disappear completely.<sup>26,29</sup>

Whereas there are few precipitates in as-grown Ni or Co-doped crystals, the reverse is true for lithium-doped MgO crystals. The lithium impurities are present mostly as Li<sub>2</sub>O precipitates with some present as isolated substitutional Li<sup>+</sup> ions.<sup>30,31</sup> Oxidation of MgO:Li crystals above 1100 K disperses lithium ions from the precipitates and forms [Li]<sup>0</sup>

centers around the precipitates.<sup>31</sup> The structure of this defect in the linear  $\langle 100 \rangle$  axial direction is O<sup>2-</sup>-Li<sup>+</sup>-O<sup>-</sup>, where Li<sup>+</sup> is a substitutional cation and O<sup>-</sup> represents a hole trapped at an adjacent O<sup>2-</sup> ion.<sup>31–33</sup> This [Li]<sup>0</sup> defect absorbs light at 690 nm (1.8 eV).<sup>31</sup> The absorption coefficient of the [Li]<sup>0</sup> band at 1.8 eV is a measure of the amount of Li<sup>+</sup> ions around the Li<sub>2</sub>O precipitates.<sup>31</sup> They are stable up to 700 K in air.<sup>34</sup>

MgO is an ionic insulator with a band gap of 7.8 eV and can accommodate many energy levels of defects. It is transparent at all commercially available UV wavelengths, in the visible region and in a wide part of the IR region. As a consequence laser interactions are dominated by absorption at defects. The emission lines of an argon laser are absorbed by oxidized MgO:Li crystals and in Co or Ni-doped crystals after TCR. Strong absorption of the laser emission may heat the crystals to temperatures sufficiently high to induce precipitation of impurities or to dissociate precipitates already present in the crystals. One important advantage of the laser-induced phase changes compared to furnace anneals is that the laser can produce coloration or decoloration of the samples in localized regions and thus imprinting or erasing is, in principle possible.

In this paper we demonstrate (1) laser-induced dissociation and formation of precipitates in lithium-doped MgO crystals and the results are compared with furnace anneals, (2) dissociation of metallic colloids in MgO crystals doped with either cobalt or nickel. One important difference with previously reported experiments on annealing out of precipitates in implanted materials<sup>7–19</sup> is that, in the latter, the impurity diffusion occurs in a region very close to the surface of the crystal, with an outmost thickness of the order of 1 μm, while in the present work these phenomena take place

on a much larger scale with crystal thicknesses of the order of a millimeter.

## II. EXPERIMENTAL PROCEDURE

Magnesium oxide crystals doped with Li, Co, or Ni used in this investigation were grown at the Oak Ridge National Laboratory by an arc-fusion technique<sup>35</sup> using high-purity MgO powder from Kanto Chemical Chemistry, Tokyo, Japan. The lithium concentration was determined by spectrographic analysis to be 400 ppm. The cobalt and nickel concentration was measured by neutron activation analysis to be  $\sim 2100$  and  $\sim 4000$  ppm, respectively. Single-crystal specimens having  $\{100\}$  faces were cleaved from ingots in the boule. The samples were first mechanically polished to remove cleaving steps. The damaged surface was removed by chemical polishing in hot phosphoric acid maintained at about 370 K.

Two types of thermochemical reduction were employed. One involved reduction in a high-purity graphite capsule inserted in the hot zone of a horizontal alumina tube furnace surrounded by flowing nitrogen gas. The temperatures were typically 1673 K. A more severe reduction was performed by enclosing the samples in an evacuated tantalum chamber heated to temperatures of about 2400 K under a high pressure of magnesium vapor ( $\sim 7$  atm), followed by rapid cooling.

Near-infrared, visible, and UV optical absorption measurements were made in a Perkin-Elmer, Lambda 19 spectrophotometer. The irradiations were performed in air with a Beam-Lok 2080 Spectra Physics Ar<sup>+</sup> laser operating in the visible multiline mode that includes several visible lines, the most intense occurring at 514 nm (10 W) and 488 nm (8 W), respectively. Under these conditions the maximum nominal power of the laser emission is 22 W. The target of the incident light beam on the sample was  $\sim 5$  mm<sup>2</sup>. The laser was operated in the continuous mode for time intervals of the order of tenths of minutes; hence, the photon fluences absorbed by the samples were typically four orders of magnitude smaller than in pulsed experiments,<sup>7-19</sup> although the total energy absorbed during the treatment time is much higher. The transmitted laser light through the samples was measured with a Spectra Physics power meter. Occasionally the samples were heated during irradiation inside a horizontal, axial hole of a furnace. All our experiments were performed near the threshold temperature for aggregation and dissociation of precipitates.

## III. EXPERIMENTAL RESULTS AND DISCUSSION

The results of the three dopants (lithium, cobalt, and nickel) in MgO single crystals will be treated individually.

### A. MgO:Li crystals

As-grown lithium doped MgO crystals exhibit an amber coloration due to the 2.6 eV (477 nm) and 3.8 eV (326 nm) absorption bands attributed to trace Ni<sup>3+</sup> ions<sup>36</sup> inadvertently introduced during crystal growth; the latter is not pronounced in Fig. 1. The band at 4.3 eV (280 nm) is associated with the Fe<sup>3+</sup> charge transfer band.<sup>37,38</sup> To a greater or lesser extent all MgO starting powders contain Fe impurities. In

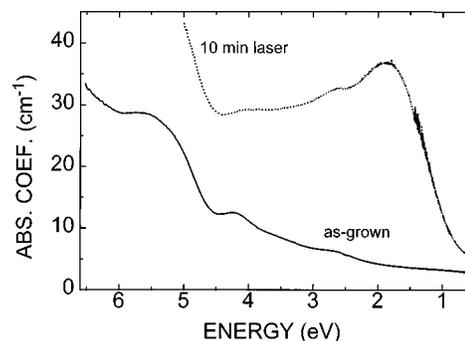


FIG. 1. Optical-absorption spectra of a MgO:Li crystal: as-grown (bottom) and after 10 min of laser irradiation at  $P=18$  W (top).

these crystals the concentration was estimated to be 4 ppm.<sup>39</sup> In the as-grown crystals lithium ions were the major impurity. They were present primarily as Li<sub>2</sub>O precipitates, with some substitutional lithium ions randomly distributed in the crystal.<sup>34</sup>

### 1. Dissociation of Li<sub>2</sub>O precipitates

In an as-grown MgO:Li crystal, the two Ar<sup>+</sup> laser lines at 514 and 488 nm (2.41 and 2.54 eV) lines were absorbed by the 2.6 eV Ni<sup>3+</sup> absorption band. After a sample was irradiated with laser power of 18 W for a few seconds in air, the local temperature of the irradiated region across the crystal rapidly increased. The thermal stress often produced cracks, followed by blue coloration. The coloration increased with irradiation, and after several minutes the sample exhibited a dark blue coloration (Fig. 1, top). The coloration is due to a broad absorption band centered at 1.8 eV. The defect responsible for this band has been previously identified as the [Li]<sup>0</sup> center. As noted this defect can also be produced by oxidation at high temperatures.<sup>31</sup> In either case, the appearance of the blue coloration indicates that Li<sup>+</sup> ions were dissociated from Li<sub>2</sub>O precipitates during irradiation, and are concentrated around the precipitates, forming [Li]<sup>0</sup> centers.

We know from a previous study<sup>40</sup> that for a low dislocation density sample ( $\leq 10^5$  cm<sup>-2</sup>) there exists a threshold temperature for the dissociation of Li<sup>+</sup> ions from Li<sub>2</sub>O precipitates to form stable [Li]<sup>0</sup> centers in an oxygen atmosphere. This threshold temperature is 1160 K. However, when the dislocation density becomes excessive, such as in the surface region of cracked, cleaved or abraded surfaces, the dislocations propagate  $\sim 1$  mm into the inner region at elevated temperature.<sup>40</sup> These dislocations serve to enhance the dissociation of Li<sup>+</sup> ions and lower the temperature at which [Li]<sup>0</sup> centers are formed. A subthreshold temperature of 1050 K has been observed.<sup>40</sup>

In the present study we note that cracking is a necessary condition for the coloration process to initiate near the threshold. Samples in which cracks were not observed remain amber in color even after 30 min irradiation. To verify that cracks initiate the blue coloration, as-grown samples were intentionally fractured along cleavage planes by heating them at  $\sim 500$  K and rapidly quenched in water. This treatment produced several cracks that penetrated from one surface to another. After a few seconds of irradiation at 18 W, the blue coloration was observed in all the quenched

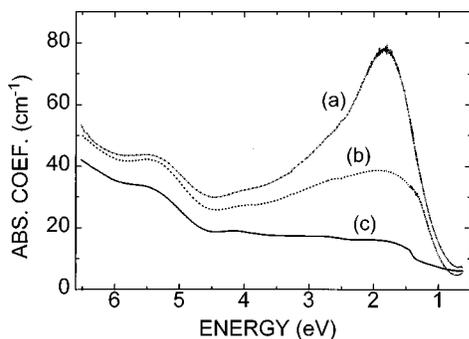


FIG. 2. Optical-absorption spectra for (a) an oxidized MgO:Li crystal at 1373 K for 30 min and after laser irradiation for (b) 15 min and (c) 30 min.

samples. On the other hand, when samples were either abraded with SiC-120 paper or scratched with a diamond-tipped pen and then laser irradiated with 18 W, no significant blue coloration was observed. These results indicate that there exists a difference in the rate of  $[\text{Li}]^0$  formation, even though both the cracked region in the interior of the quenched crystals and the abraded surfaces have high dislocation densities. We attribute the difference to temperature gradient, the surface being cooler.

## 2. Formation of precipitates

We now show that laser irradiation can cause the reverse effect, namely, the formation of  $\text{Li}_2\text{O}$  precipitates at the expense of  $[\text{Li}]^0$  centers.  $[\text{Li}]^0$  centers were produced in several MgO:Li samples by heating in flowing oxygen at  $\sim 1373$  K for 30 min. The samples exhibited the characteristic blue coloration due to  $[\text{Li}]^0$  centers (Fig. 2). Laser irradiation at 12 W was performed. Decoloration occurred only when a crack was formed, and started at the cracks (Fig. 3). It rapidly progressed with time until the sample recovered the initial amber color. The optical progression is shown in Fig. 2. The loss of the blue coloration suggests that  $\text{Li}^+$  ions from  $[\text{Li}]^0$  centers recondensed at the  $\text{Li}_2\text{O}$  precipitates. The preferential decoloration along the cracks supports (1) the contention that mobility of  $\text{Li}^+$  ions is enhanced at regions of high dislocation density, such as along cracks,<sup>41</sup> and (2) the reverse process, namely, recondensation, can also be enhanced by dislocations.

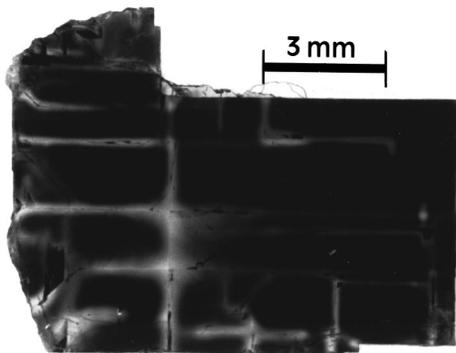


FIG. 3. Transmission optical photograph of a MgO:Li sample oxidized at 1373 K for 30 min and laser irradiated. Cracks were formed and  $[\text{Li}]^0$  centers were preferentially annealed out along the cracks.

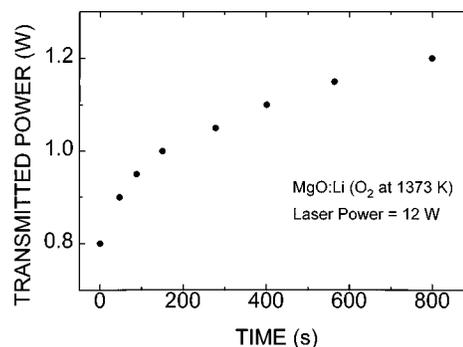


FIG. 4. Laser transmitted power versus time for a MgO:Li sample previously oxidized at 1373 K for 30 min.

The formation of  $\text{Li}_2\text{O}$  precipitates was also monitored with power-meter measurements of the laser light transmitted through the sample. As the formation of  $\text{Li}_2\text{O}$  precipitates progresses during irradiation, the intensity of the  $[\text{Li}]^0$  absorption band at 1.8 eV decreased and the intensity of the laser transmitted light increased. This technique provides the advantages of an *in situ* measurement. Figure 4 shows a plot of the transmitted power against time for a sample oxidized at 1373 K for 30 min in which cracks were produced by immersion in water. From this curve, the cross section for the dissociation of  $[\text{Li}]^0$  centers can be determined using the relationship  $\sigma = (\Delta C/C)/\Delta \phi$ , where  $C$  is the initial concentration of  $[\text{Li}]^0$  centers and  $\Delta C/\Delta \phi$  is the loss of  $[\text{Li}]^0$  per cubic centimeter for a given irradiation dose  $\Delta \phi$ , which is the number of photons per unit area.  $\Delta \phi$  is calculated by dividing the energy deposited per unit area by 2.6 eV. Assuming that  $\Delta C/C$  is equal to the fractional decrease of the 1.8 eV band, or the increase of the transmitted power, the cross section can be determined from the initial slope of the curve in Fig. 4. The resulting value was  $\sigma \sim 0.2$  bs, which is several orders of magnitude smaller than that determined for radiation induced diffusion of lithium under irradiation by electrons<sup>34</sup> or  $\gamma$  rays.<sup>42</sup> This indicates that laser-induced lithium diffusion is a thermal process.

## B. MgO:Co crystals

### 1. Reduction and oxidizing treatments

Optical-absorption measurements were used to monitor the presence of metallic cobalt precipitates. In as-grown MgO:Co crystals two bands have been observed at  $\sim 2.4$  and  $\sim 4.3$  eV.<sup>24</sup> The former band has been attributed to  $d \rightarrow d$  transitions of  $\text{Co}^{2+}$  ions,<sup>43</sup> and the latter to the  $\text{Fe}^{3+}$  charge-transfer band.<sup>37,38</sup> The iron concentration was estimated to be 50 ppm.<sup>39</sup> The initial pink coloration of these crystals turned dark after thermochemical reduction at  $\sim 1573$  K for 1 h. A broad extinction band was observed at  $\sim 3.7$  eV, similar to that observed in crystals reduced at much higher temperatures and pressures,<sup>24</sup> in which coherent precipitates made of fcc cobalt in the  $\beta$  phase were identified.<sup>24</sup> The fact that the band at 2.4 eV remained almost unchanged indicated that only a small fraction of the  $\text{Co}^{2+}$  ions had been reduced to cobalt precipitates. Indeed, visual observation of the sample cross section confirmed that the dark coloration due to cobalt precipitates was confined to the surface regions only.

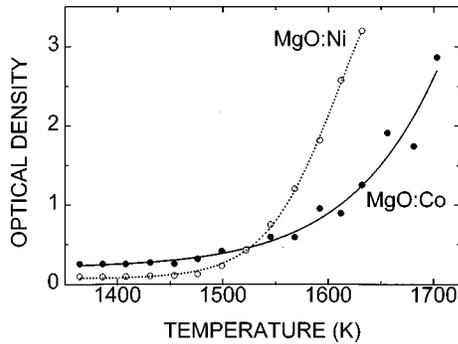


FIG. 5. Optical densities produced at different temperatures of the 3.7 and 2.2 eV bands in MgO:Co and MgO:Ni crystals, respectively.

The formation of the broad extinction band at 3.7 eV was investigated by reducing a MgO:Co sample for 10 min intervals at increasing furnace temperatures with increments of 25 K. The optical densities versus temperature are plotted as solid circles in Fig. 5. A threshold temperature for the band formation was estimated to be 1500 K. In order to study the thermal stability of this band, a sample previously reduced at 1573 K for 1 h was isochronally annealed for 10 min intervals at increasing temperatures in flowing oxygen. The loss of the extinction at 3.7 eV did not begin to occur until about 1325 K, indicating that the colloids start to dissociate at this temperature.

An activation energy for the dissociation of the precipitates was determined. Three pieces of the same crystal reduced, at 1573 K for 1 h, were isothermally annealed at 1325, 1365, and 1405 K. After each anneal, the optical densities of the 3.7 eV band were plotted against time in Fig. 6. Using the cross-cut method on these curves an activation energy of  $\sim 3.0$  eV was obtained.

## 2. Laser-induced dissociation of precipitates

Dissociation of cobalt precipitates can also be induced by annealing with an Ar laser at 12 W. A MgO:Co sample previously thermochemically reduced at 1673 K for 1 h was laser irradiated at 10 min intervals. The optical absorption spectra were measured after each irradiation. The resulting optical spectra are shown in Fig. 7. The top curve represents the spectrum of the crystal after thermochemical reduction. The subsequent observed loss of coloration shown in the

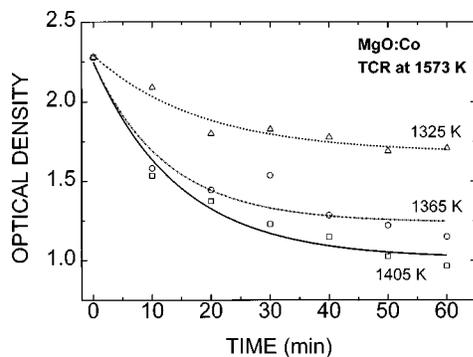


FIG. 6. Optical density versus time at three temperatures for MgO:Co crystals previously reduced at 1573 K for 1 h.

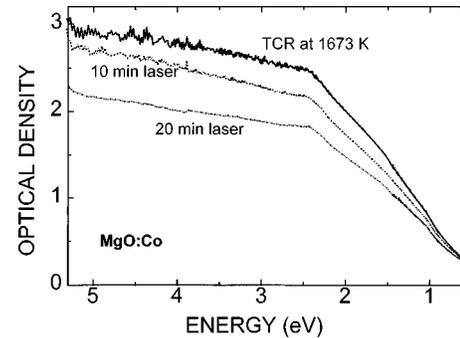


FIG. 7. Optical absorption spectra of a MgO:Co crystal reduced at 1673 K for 1 h (a) before and after subsequent laser annealing at  $P=12$  W for (b) 10 min and (c) 20 min. The sample was placed inside a furnace at 473 K.

lower curves indicates that the cobalt precipitates created during the thermochemical reduction process were dissociated by the laser annealing.

In contrast with the laser irradiations performed in MgO:Li crystals, no cracking occurred in MgO:Co crystals unless the beam is focused to one small spot. Unlike MgO:Li crystals, cracks are not a prerequisite for aggregation or dissociation of precipitates. Dissociation of precipitates depends on laser power and sample temperature. These conditions permit us to estimate the activation energy for precipitate dissociation by laser. Unfortunately, determination of the temperature at the irradiated region is not feasible. Therefore an accurate measurement of the activation energy is not possible. However, we can make an estimation.

(a) *Optical-absorption measurements.* It was observed that 12 W was the minimum power which produces the decoloration of a crystal at 300 K. We will assume that this power corresponds to the threshold temperature for precipitate dissociation ( $T \sim 1325$  K). Three crystals, similarly reduced, were also irradiated at 12 W for 10 mins at three temperatures: 300, 400, and 500 K. They were placed inside the horizontal axial hole of a furnace. The decrease in optical density was plotted versus time (Fig. 8). Assuming that the activation energy in this case is also 3.0 eV, the temperatures in the irradiated regions of the latter two samples can be estimated. The resulting values are  $\sim 1401$  and  $\sim 1454$  K, respectively, which are within the expected temperature range. We conclude from these results that *the laser-induced dissociation is a thermal process.*

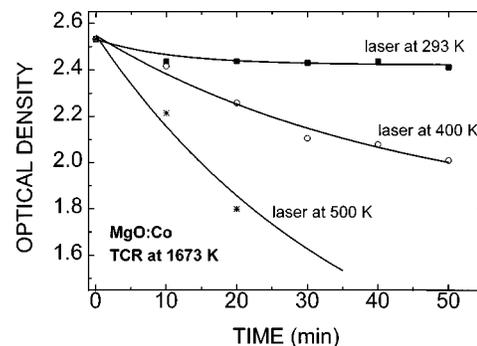


FIG. 8. Optical densities of three MgO:Co crystals reduced at 1673 K for 1 h and laser-irradiated inside a furnace at (a) RT, (b) 400 K, and (c) 500 K.

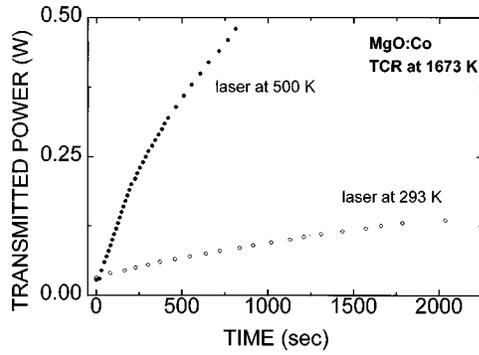


FIG. 9. Laser-transmitted light from two pieces of the same MgO:Co crystal reduced at 1673 K for 1 h. The samples were placed inside a furnace at (a) 300 K and (b) 500 K.

(b) *In situ transmitted power measurements.* The dissociation of Co precipitates was also monitored with power-meter measurements of the transmitted laser light. As the dissociation of Co precipitates progressed during irradiation, the transmitted light increased because extinction at 3.7 eV diminished. Figure 9 is a plot of the time dependence of the transmitted power for two temperatures. The samples were irradiated with a laser power of 12 W inside the horizontal axial hole of the furnace maintained at 300 and 500 K, respectively. Assuming that in this case the activation energy is also 3.0 eV, if the sample at 300 K corresponds to the threshold temperature for dissociation at 1325 K, then the sample at 500 K corresponds to 1451 K, which agrees very well with  $T=1454$  K determined above. From the initial slopes of these curves, the corresponding cross sections were determined to be 0.01 and 0.2 bs, respectively. These values indicate that the cobalt diffusion occurs via a thermal process rather than a radiation induced diffusion process.

Thickness effect was also investigated. Several samples with thicknesses ranging from 0.5 to 2 mm were first thermochemically reduced at 1600 K for 30 min and then laser irradiated to dissociate the precipitates. It was concluded that the laser power necessary to induce decoloration of the sample increases with the sample thickness. The reason for this observation is that precipitates were confined to the surface regions only, as Fig. 10 demonstrates. The initial thickness ( $\sim 0.85$  mm) of a thermally reduced crystal was diminished by successive polishings of the crystal on the same face. The optical density at 3.7 eV is plotted versus sample

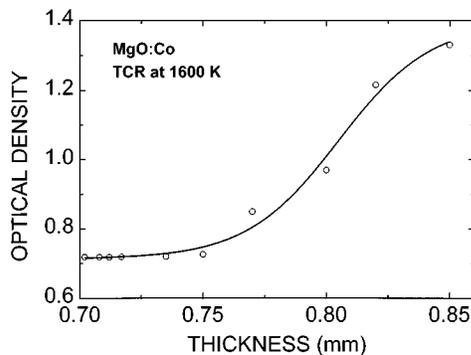


FIG. 10. Optical density versus thickness for a MgO:Co crystal reduced at 1600 K for 30 min.

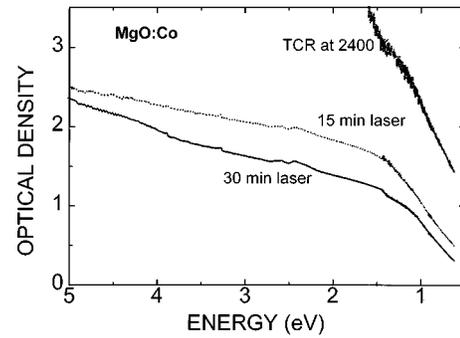


FIG. 11. Optical absorption spectra of a thermochemically reduced MgO:Co crystal at 2400 K (a) before and after laser annealing for (b) 15 min and (c) 30 min. The laser power was 10 W.

thickness (Fig. 10). The absorption coefficient decreases vary rapidly at the edge, and remains practically unchanged after removing 0.1 mm of the surface. Precipitates are mainly concentrated at both surfaces within a depth of  $\sim 0.1$  mm. If the sample is thin ( $\sim 0.5$  mm), the separation between both regions is small and the net temperature is higher. In thick samples, the separation between these two regions is large and additional laser power is needed to reach the threshold temperature for precipitate dissociation.

Crystals thermochemically reduced under much more severe conditions ( $T\sim 2400$  K in  $\sim 7$  atm of Mg vapor) were also laser irradiated at 10 W for 10 min intervals. The extinction of such a crystal is much more severe than one thermochemically reduced in graphite at lower temperatures, see top of Fig. 11. The two lower curves are spectra after irradiation. Transmitted laser power measurements were also performed. The results indicate that cobalt precipitates are dissociated at about the same rate during either reduction process once a threshold temperature is reached.

Cracking was produced when laser operating at 10 W was focused to a small spot. Associated with the crack formation is the observation of sparks in that area. After cooling, the irradiated area appeared “etched,” and a significant amount of material has been removed, indicating that a photoablation process has occurred. In ionic crystals, concentrated beam followed by rapid cooling can produce highly defective surfaces. Ejection of atomic fragments from the surface results in bulk defects that are predominantly vacancies.<sup>1-6</sup> Laser-induced desorption and ablation of species from the MgO surface are greatly enhanced by lattice defects.<sup>1-6</sup> The defect concentration is very high in the cracked areas thus facilitating the ion desorption.

## C. MgO:Ni crystals

### 1. Reduction and oxidizing treatments

After thermochemical reduction of nickel-doped MgO crystals, a broad extinction centered at  $\sim 2.2$  eV was observed, which was qualitatively similar to that reported earlier.<sup>21,22</sup> This extinction has previously been associated with coherent nickel precipitates.<sup>21,22</sup> We shall associate the extinction with Mie scattering from precipitates. As in MgO:Co crystals, the dark coloration was confined to the surface regions only. A MgO:Ni sample was thermochemically reduced in graphite for 10 min intervals at increasing

temperatures. The optical density enhancement at 2.2 eV with temperature is plotted as curve *B* in Fig. 5. A threshold temperature for the band formation was determined to be  $\sim 1500$  K.

In order to determine the thermal stability of the precipitates, we subjected a TCR crystal to oxidation at high temperatures; a sample previously thermochemically reduced at 1673 K for 1 h was isochronally annealed for 10 min intervals at increasing temperatures in flowing oxygen. The loss of the extinction at 2.2 eV did not begin to occur until about 1325 K, indicating that the colloids start to dissociate at this temperature.

To determine the activation energy, three similar crystals were isothermally annealed at 1350, 1400, and 1450 K in flowing oxygen. Following the same procedure as described earlier, an activation energy of  $\sim 1.9$  eV was obtained. The smaller activation energy for nickel precipitate dissociation compared to that of cobalt precipitates may be due to the smaller ionic radius of  $\text{Ni}^{2+}$  ions, attended by ease of diffusion.

### 2. Laser-induced dissociation of precipitates

Similar to MgO:Li crystals, laser-induced dissociation of the nickel precipitates was achieved after a crack was created. In samples where cracks were produced by quenching in water, the decoloration was enhanced. On the other hand, surfaces abraded with emeryl paper did not enhance the precipitate dissociation. In crystals TCR at  $\sim 2400$  K and therefore containing a high concentration of precipitates, they seemed to be thermally more stable. Dissociation occurred only when the samples were simultaneously heated in a furnace at 773 K and laser irradiated with 12 W, as compared with 300 K and 12 W for those TCR at lower temperatures.

The reason for the stability of precipitates from TCR at 2400 K may be due to the high concentration of precipitates in any given region. Transmission electron microscopy observations showed that precipitates were very inhomogeneously distributed. Regions with a high concentration of precipitates were separated by regions that were almost free from precipitates.<sup>21,22,24,25</sup> Also, the nickel content in MgO:Ni crystals was twice that of cobalt in MgO:Co crystals. We conjecture that in regions of high concentration, the short migration distance does not provide many sites that the ions can occupy. However, when the sample is simultaneously irradiated and heated in a furnace, the ion mobility increases, thus facilitating the nickel ion dispersion. There must be a threshold temperature that is more than the laser alone can produce.

High concentration of the laser beam can imprint different patterns in MgO:Ni containing nickel colloids. Focusing the laser and operating at powers higher than 10 W, cracks were produced. To minimize cracking, the sample was heated to 773 K and laser irradiated, so as to decrease the thermal gradient. In a crystal TCR at  $\sim 2400$  K and placed in the furnace at 773 K, the letter *L* was written with the laser operating at 17 W (Fig. 12). Imprinting can also be done in thermochemically reduced MgO:Co crystals.

## IV. SUMMARY AND CONCLUSIONS

Impurity precipitation and dissociation of precipitates were induced both by purely thermal means and by laser

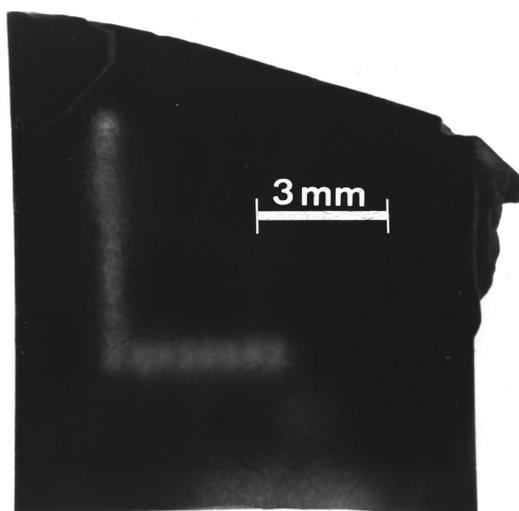


FIG. 12. Transmission optical photograph of a thermochemically reduced MgO:Ni sample at 2400 K and laser irradiated inside a furnace at 773 K. The letter ‘L’ was inscribed with the laser and corresponds to the region where nickel colloids were dissociated.

irradiation in MgO single crystals doped with Li, Co, or Ni. The precipitate concentrations were monitored primarily by the extent of Mie scattering. Laser irradiation was made with an  $\text{Ar}^+$  laser operating in the continuous mode for time intervals of the order of minutes.

In MgO:Li crystals, oxidation at  $T > 1100$  K dispersed lithium ions from  $\text{Li}_2\text{O}$  precipitates to form  $[\text{Li}]^0$  centers. The absorption band of this center at 1.8 eV was used to monitor the concentration of the dispersed ions. Laser-induced experiments showed that both lithium precipitation and dispersion was enhanced by the presence of cracks. A cross-section value of 0.2 bs was obtained for Li displacement, indicating that the diffusion of lithium occurs via a thermal process rather than a radiation induced diffusion, as in the case of ionizing irradiation.<sup>34,42</sup>

In MgO:Co crystals, metallic colloids were produced by thermochemical reduction at elevated temperatures that resulted in a broad extinction band at 3.7 eV due to Mie scattering from the precipitates. This band was used to monitor the presence of colloids in the samples. An activation energy of 3.0 eV was obtained for a purely thermal process for precipitate dissociation. A cross-section value of 0.01 bs was determined for the dissociation of cobalt ions. Investigations on thickness effects showed that the laser power needed to induce dissociation of the colloids increases with the sample thickness. When the laser was focused on the surface of the crystal, laser-induced desorption and ablation was observed.

Experiments involving aggregation and dissociation of nickel ions were also performed in nickel-doped MgO crystals. An activation energy of 1.9 eV was determined for the dissociation of Ni ions. Different patterns were imprinted with high concentration of the laser beam.

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