



# Dynamics of $F$ -center annihilation in thermochemically reduced MgO single crystals

A.I. Popov<sup>a,d</sup>, M.A. Monge<sup>a,\*</sup>, R. González<sup>a</sup>, Y. Chen<sup>b</sup>, E.A. Kotomin<sup>c,d</sup>

<sup>a</sup>Departamento de Física, Escuela Politécnica Superior, Universidad Carlos III, Avda de la Universidad, 30, 28911 Leganés, Madrid, Spain

<sup>b</sup>Division of Materials Sciences, Office of Basic Energy Sciences, Sc 13, Germantown, MD 20874-1290, USA

<sup>c</sup>Max-Planck Institut für Festkörperforschung, Heisenberstr. 1, Stuttgart 70569, Germany

<sup>d</sup>Institute for Solid State Physics, University of Latvia, Kengaraga 8, Riga, LV-1063, Latvia

Received 16 October 2000; accepted 15 January 2001 by P. Burler

## Abstract

Optical absorption measurements were used to monitor the thermal annihilation of oxygen vacancies ( $F$ -centers) in thermochemically reduced MgO crystals. The annihilation characteristics were sample-dependent and varied strongly with the  $F$ -center concentration. Different mechanisms for the destruction of  $F$  centers are suggested depending on their concentration. © 2001 Elsevier Science Ltd. All rights reserved.

**Keywords:** A. Insulators; C. Point defects; D. Optical properties; E. Optical absorption

**PACS:** 61.72.C; 78.40; 61.72.J

## 1. Introduction

Anion vacancies in magnesium oxide are observed in two charge states:  $F$ , or  $F^+$  centers (oxygen vacancies occupied by two or one electron, respectively). The paramagnetic  $F^+$  center is characterised by both electron paramagnetic resonance and optical absorption spectroscopy [1–9]. The diamagnetic  $F$  center is inferred from the magnetic and optical properties of the  $F^+$  center. The  $F$  and  $F^+$  centers both absorb at essentially the same energy: 5.01 and 4.92 eV, respectively [2].

$F$ -type centers in MgO can be produced principally by two methods: irradiation with energetic particles, such as neutrons, electrons or ions [1–7,10,11] and thermochemical reduction performed under severe reducing conditions resulting in stoichiometric deficiency in the oxygen sublattice [2,7,12–14]. Typically the sample is enclosed in a tantalum chamber containing several atmospheres of Mg vapour at  $T > 2000$  K.

The major differences in anion vacancies created by irra-

diation and TCR are as follows: in neutron or ion-irradiated crystals the anion vacancies exist normally in the  $F^+$  state [6,7], unless stimulated by photons or charged particles. In thermochemically reduced (TCR) crystals, the anion vacancies prefer to be in the neutral  $F$  state unless excited by photons or charged particles [12,14]. In electron-irradiated MgO the situation is intermediate: both  $F$  and  $F^+$  are produced [5,15]. In irradiated crystals, the interstitials become mobile and recombine with the vacancies at temperatures not much higher than room temperature. In MgO, the interstitials become mobile at about 400 K. In contrast, annihilation of  $F$  centers in TCR samples requires temperatures in excess of 1300 K [2,14,16,17]; oxygen vacancies are created non-stoichiometrically and have no oxygen interstitials to recombine with. They are therefore much more stable.

Analysis of the  $F$ -center annealing curves in TCR MgO crystals indicates that the annihilation temperature and the activation energy depend on both the  $F$  center and  $[H^-]^+$ -ion (a proton with two electrons occupying an oxygen-vacancy site, which is therefore positively charged as denoted by the superscript) concentrations [14].  $F$  center isochronal annealing in MgO containing high concentrations of  $[H^-]^+$  centers ( $>10^{17}$  cm<sup>-3</sup>) indicates activation energy values higher than 4.0 eV [14]. In MgO crystals

\* Corresponding author. Tel.: +349-1-624-94-14; fax: +349-1-624-94-30.

E-mail address: mmonge@fis.uc3m.es (M.A. Monge).

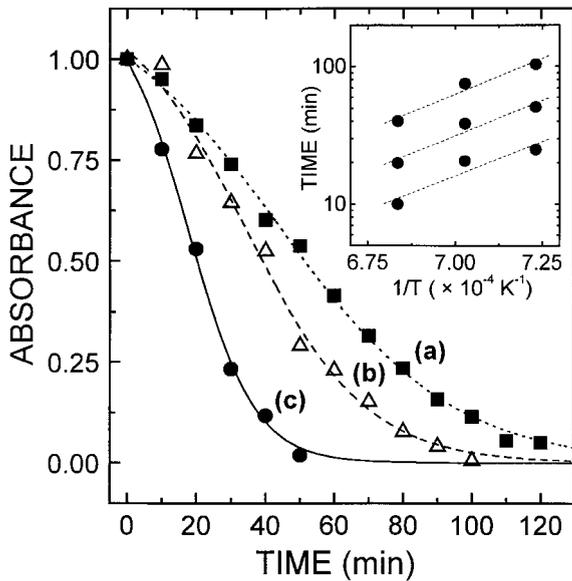


Fig. 1. Absorbance vs annealing time at (a) 1383 K, (b) 1423 K and (c) 1463 K, for sample MgO I with initial  $F$ -center concentration of  $5 \times 10^{16} \text{ cm}^{-3}$ . A semilog plot of the time to reach a constant absorbance versus  $T^{-1}$  for the three crystals is shown in the inset.

with  $F$ -center concentrations of about  $10^{17} \text{ cm}^{-3}$  and low  $[\text{H}^-]^+$ -centers ( $< 10^{17} \text{ cm}^{-3}$ ), the reported values for the activation energy derived from isothermal or isochronal anneals of the  $F$  band are 3.4 and 3.0 eV, respectively [17–19].

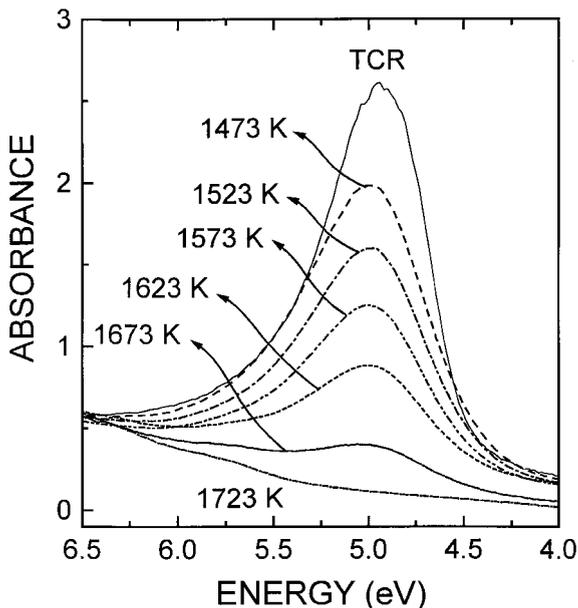


Fig. 2. Optical absorption spectra for sample MgO II ( $F$  concentration  $\approx 2 \times 10^{17} \text{ cm}^{-3}$ ) at several selected annealing temperatures.

In the present work, thermal annihilation of  $F$ -centers in TCR crystals was studied by optical absorption measurements in three MgO crystals, in which the  $F$  concentration varied by two orders of magnitude and the concentration of the  $[\text{H}^-]^+$  centers is less than  $10^{17} \text{ cm}^{-3}$ . Different mechanisms for the destruction of  $F$ -centers in different concentrations are discussed.

## 2. Experimental procedures

The MgO crystals used were grown at the Oak Ridge National Laboratory using the arc fusion technique [20]. The starting material was MgO powder from the Kanto Chemical Company, Japan. The impurity concentrations have been reported elsewhere [20]. The total impurity content is about 100 ppm. The main impurities are Ca, Si, P, Al, Fe, and Cr with concentrations of 50, 20, 13, 10, 7 and 1 ppm, respectively. TCR was performed in a tantalum chamber at  $\approx 2400 \text{ K}$  and  $> 7 \text{ atm}$  of magnesium vapour and followed by rapid cooling. Subsequent reducing heat treatments of the TCR samples were made inside a graphite container inserted in a horizontal furnace with flowing high-purity nitrogen gas. Optical absorption measurements in the UV-VIS-IR were made with a Perkin-Elmer Lambda 19.

## 3. Results and discussion

Results on  $F$ -center annihilation are presented for three TCR crystals, labeled MgO I, MgO II, and MgO III, with very different concentrations of  $F$  centers. The  $F$ -center concentrations in these samples were estimated from the experimentally deduced relationship [21]

$$n(F) = 5 \times 10^{15} \alpha(F), \quad (1)$$

where  $n(F)$  denotes the concentration of anion vacancies and  $\alpha(F)$  is the absorption coefficient of the 250 nm band. The resulting concentrations were  $5 \times 10^{16}$ ,  $2 \times 10^{17}$  and  $6 \times 10^{18} \text{ cm}^{-3}$ , respectively. The  $[\text{H}^-]^+$  concentrations in all three samples were lower than  $10^{17} \text{ cm}^{-3}$ .

The activation energy for the annihilation of the  $F$  centers in sample MgO I was obtained using the cross-cut method [22]. This sample, which had the lowest  $F$  concentration, was cleaved in three pieces with the same thickness ( $t = 1.5 \text{ mm}$ ), each of which had the same  $F$ -center concentration. These crystals were then isothermally heated for 5 min at 1383, 1423 and 1463 K, respectively, in a reducing atmosphere. After each anneal, the absorbance of the corresponding  $F$ -band was measured and plotted as a function of time (Fig. 1). In the inset the times for the three crystals to reach the same arbitrary absorbance value are plotted against the reciprocal to the annealing temperature  $1/T$ . The activation energy is found to be  $1.9 \pm 0.2 \text{ eV}$ .

Sample MgO II, with an intermediate  $F$ -center concentration, was isochronally annealed for 5-min duration at increasing temperatures of 50 K intervals in a reducing

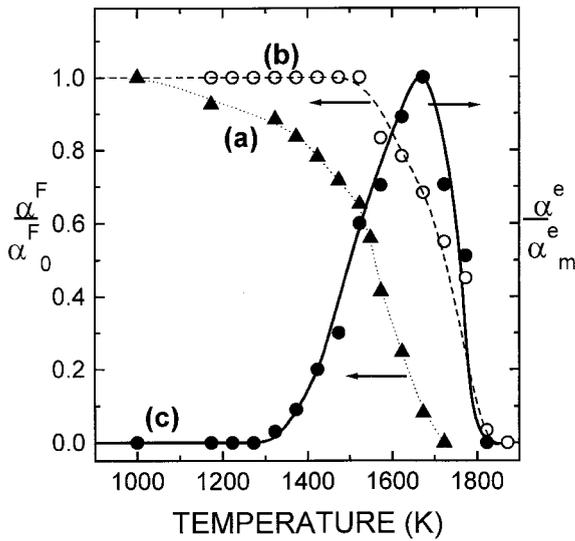


Fig. 3. Normalised concentration of (a)  $F$ centers in sample MgO II, (b)  $F$ centers in sample MgO III, and (c) 3.59–3.35 eV absorption band in MgO III against isochronal annealing temperature.

atmosphere. Fig. 2 shows the absorption spectra after heating at selected temperatures. The most pronounced absorption occurred at 5.0 eV. The net effect of the annealing was the decrease of the  $F$ -center concentration. Dimers such as  $F_2$ , which absorbs at 3.5 and 1.5 eV, and  $F_2^{2+}$ , which absorbs at 3.8 eV, respectively, were not

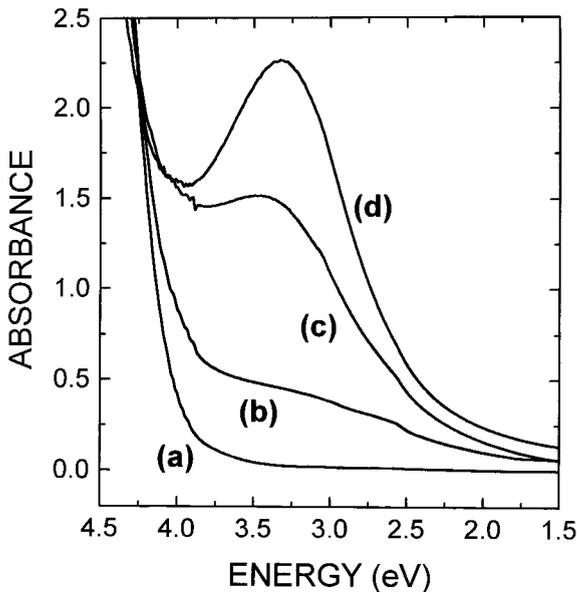


Fig. 4. Optical absorption spectra in sample MgO III: (a) TCR, and after thermal annealings at (b) 1373 K (c) 1573 K and (d) 1673 K. The peak position of the 3.59–3.35 eV absorption band was obtained by deconvoluting the corresponding absorption spectrum.

observed [1,2,4,7,23,24]. The normalised concentration of  $F$ -centers vs isochronal annealing temperature is shown in Fig. 3. The  $F$  concentration begins to decrease after the anneal at 1200 K.

The annihilation of mobile  $F$ -centers may occur either at internal defects, impurities and traps (such as dislocations and grain boundaries) when the  $F$ -center concentration is low, or at the external surfaces when the  $F$ -center concentration is high. The diffusion-controlled kinetics in the first case is described by a standard rate equation

$$\frac{dC_F(t)}{dt} = -KC_F(t)C_T, \quad (2)$$

where  $C_F(t)$  is the  $F$ -center concentration, the reaction rate is  $K = 4\pi Dr_0$  ( $D$  is the diffusion coefficient,  $D = D_0 \exp(-E_a/kT)$ ,  $E_a$  is the  $F$ -center migration energy,  $r_0$  is the reaction radius), and  $C_T$  is the concentration of traps where the  $F$ -centers annihilate.

If  $C_T \gg C_F$ , a first-order kinetics takes place and the concentration decay is exponential in time. The alternative kinetics when the  $F$ -centers annihilate at the sample surface has been discussed in Ref. [25]. The  $F$ -center concentration at time  $t$  is

$$C_F(t) = \frac{8C_0}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp\left(-Dt\pi^2 \frac{(2n+1)^2}{4d^2}\right), \quad (3)$$

where  $C_0$  is the initial  $F$ -center concentration and  $2d$  is the sample thickness.

After a short transient period, the first term in Eq. (3) starts to dominate, which again results in the first order kinetics

$$C_F(t) \propto \exp(-DtB), \quad (4)$$

but now with a well defined co-factor  $B = \pi^2/(4d^2)$ . Using Eq. (4), the migration activation energy in sample MgO II was estimated to be  $2.5 \pm 0.1$  eV.

The normalised  $F$ -center annihilation for Samples II (intermediate  $F$  concentration) and III (high  $F$  concentration) is shown in Fig. 3, curves (a) and (b), respectively. The latter shows an unexpected result: after annealing at 1373 K, the sample developed a brown coloration due to a broad extinction band centered at 3.59 eV (345 nm), shown in Fig. 4. As the annealing temperature increased, the band became more intense, as it shifted toward lower energy. The band ultimately peaked at 3.35 eV (Fig. 4). It reached maximum intensity at 1673 K. This extinction band has been attributed to Mie scattering from nano-size cavities with typical dimensions of 3 nm, coated with magnesium metal. The normalised growth and decay of the 3.59–3.35 eV extinction band is shown as curve (c) in Fig. 3. Both the  $F$  centers and the yellow coloration vanished at 1850 K. From curve (c) and assuming a first order kinetics, an activation energy for  $F$ -center diffusion was estimated for sample III to be  $3.4 \pm 0.6$  eV, in good agreement with theoretical calculations [18,19]. For samples II and III, the pre-exponential factors of the diffusion coefficients obtained

using Eq. (4) are  $D_0 = 10^{10}$  and  $10^{12} \text{ cm}^2 \text{ s}^{-1}$ , respectively, which are many orders of magnitude larger than the typical value of  $D_0 = 10^{-3} \text{ cm}^2 \text{ s}^{-1}$  for point defects [24]. We believe this overestimation could be due to the assumption that the  $F$ -centers migrate to the surface over a distance of the order of the sample thickness ( $d = 1 \text{ mm}$ ). Assuming a  $D_0$  value of  $10^{-3} \text{ cm}^2 \text{ s}^{-1}$  and a migration energy of 3.4 eV, the mean-square displacement for the  $F$ -center can be estimated from the standard *Einstein relation*  $\langle r^2 \rangle = 6Dt$ . It gives a mean displacement smaller than 1 micrometer at 1500 K and only 10  $\mu\text{m}$  at 1800 K. Thus,  $F$ -centers are not able to reach the external surface during annealing times of 30 min; it takes a much longer time.

The thermal annealing of three samples with very different  $F$ -center concentrations, all with  $[\text{H}^-]^+$  concentrations  $< 10^{17} \text{ cm}^{-3}$ , permit us to draw certain conclusions. The key experimental observations are the following: First, the annealing rates of  $F$  centers are drastically different and are strongly dependent on the  $F$  concentration,  $C_F$ . A higher concentration has a slower rate of annihilation. Second, the sample with an exceptionally high  $C_F$  ( $6 \times 10^{18} \text{ cm}^{-3}$ ) developed a brown coloration, which we have recently attributed to magnesium-plated nano cavities based on transmission electron microscopy observations [26]. Although this concentration is higher than that in Sample II by a factor of 30, we did not observe a correspondingly less intense coloration in the latter sample.

To explain these two observations, we suggest that a direct manifestation of the intrinsic diffusion of  $F$  centers is their diffusion-controlled aggregation to ultimately form nano cavities in the temperature range of 1400–1650 K. The experimental activation energy for this process determined in sample MgO III is 3.4 eV which agrees well with the theoretical energy (3.1 eV) of the  $F$ -center elementary jump [18,19]. The activation energy values of 1.9 and 2.5 eV determined in samples MgO I and MgO II, respectively, are significantly lower and hence can not be attributed to migration of single  $F$ -centers. Thus, in samples MgO I and MgO II oxygen vacancies are annihilated either by forming dimer centers with selected impurities, which favours their joint diffusion to internal sinks (such as dislocations and grain boundaries) or with more mobile defects (such as magnesium vacancies). Indeed, a number of theoretical calculations (see [18,19,24] and references therein) agree that the migration energy of the cation vacancies is 2.0–2.4 eV and thus they could be involved in the  $F$ -center annihilation process. Both point defects and internal sinks are characteristic of the structural quality of the sample and their concentration,  $C$ , can vary from sample to sample, depending on such factors as sample growth conditions and past thermal history. Nevertheless, the results of Samples II and III indicate that  $C \approx 10^{17} - 10^{18} \text{ cm}^{-3}$ . It is not surprising that when  $C_F \ll C$ , the  $F$ -center annihilation characteristics are strongly sample dependent, giving rise to large variation in activation energies [14,17].

#### 4. Summary and conclusions

Optical absorption measurements were used to monitor the thermal annihilation of  $F$  centers in three TCR MgO single crystals with concentrations of  $5 \times 10^{16}$ ,  $2 \times 10^{17}$  and  $6 \times 10^{18} \text{ cm}^{-3}$ . The  $[\text{H}^-]^+$  concentrations in the three samples were lower than  $10^{17} \text{ cm}^{-3}$ . The annihilation rate depends on the  $F$ -concentration; the higher the concentration, the lower the rate. We propose that for crystals with a low or an intermediate  $F$  concentration ( $< 10^{17} \text{ cm}^{-3}$ ), the thermal destruction is due to more mobile defects, such as magnesium vacancies and impurities. In a sample where the  $F$ -center concentration is exceptionally high ( $> 10^{18} \text{ cm}^{-3}$ ), intrinsic diffusion and aggregation of these defects results in unusual extended defects: magnesium-plated nano cavities. Detailed theoretical analysis of these kinetics is now in progress.

#### Acknowledgements

We are indebted to V. Kuzovkov for fruitful discussions. Research at the University Carlos III was supported by the Comisión Interministerial de Ciencia y Tecnología (CICYT) of Spain and the Comunidad Autónoma de Madrid (CAM). The research of Y.C. is an outgrowth of past investigations performed at the Oak Ridge National Laboratory. A.I.P. and E.K. were partially supported by the Latvian Research Council (Grant No. 96.0666). A.I.P. acknowledges the Dirección General de Enseñanza Superior e Investigación Científica of Spain for a sabbatical grant.

#### References

- [1] B. Henderson, J.E. Wertz, *Adv. Phys.* 17 (1968) 749.
- [2] Y. Chen, R.T. Williams, W.A. Sibley, *Phys. Rev.* 182 (1969) 960.
- [3] Y. Chen, J.M. Kolopus, W.A. Sibley, *Phys. Rev.* 186 (1969) 865.
- [4] Y. Chen, W.A. Sibley, *Phil. Mag.* A 20 (1969) 217.
- [5] L.A. Kappers, R.L. Kroes, E.B. Hensley, *Phys. Rev. B* 1 (1970) 4151.
- [6] B.D. Evans, *Phys. Rev. B* 9 (1974) 5222.
- [7] B. Henderson, *CRC Crit. Rev., Solid State Mater. Sci.* 9 (1980) 1.
- [8] G.P. Summers, T.M. Wilson, B.T. Jeffries, H.T. Tohver, Y. Chen, M.M. Abraham, *Phys. Rev. B* 27 (1983) 1283.
- [9] M.C. Wu, C.M. Truong, D.W. Goodman, *Phys. Rev. B* 46 (1992) 12688.
- [10] R. González, Y. Chen, R.M. Sebek, G.P. Williams Jr., R.T. Williams, W. Gellermann, *Phys. Rev. B* 43 (1991) 5228.
- [11] R.S. Averback, P. Ehrhart, A.I. Popov, A.V. Sambeek, *Rad. Eff. Defect. S.* 136 (1995) 169.
- [12] L.A. Kappers, E.B. Hensley, *Phys. Rev.* 6 (1972) 2475.
- [13] R. González, Y. Chen, M. Mostoller, *Phys. Rev. B* 24 (1981) 6862.

- [14] Y. Chen, R. González, O.E. Schow, G.P. Summers, *Phys. Rev.* 27 (1983) 1276.
- [15] R.W. Roberts, J.H. Crawford Jr., *J. Nonmetals* 2 (1974) 133.
- [16] B.D. Evans, *J. Nucl. Mater.* 219 (1995) 202.
- [17] G.S. White, K.H. Lee, J.H. Crawford Jr., *Appl. Phys. Lett.* 35 (1979) 1.
- [18] A.I. Popov, E.A. Kotomin, M.M. Kuklja, *Phys. Status Solidi (b)* 195 (1996) 61.
- [19] R.I. Eglitis, M.M. Kuklja, E.A. Kotomin, A. Stashans, A.I. Popov, *Comput. Mater. Sci.* 5 (1996) 298.
- [20] M.M. Abraham, C.T. Butler, Y. Chen, *J. Chem. Phys.* 55 (1971) 372.
- [21] W.A. Sibley, Y. Chen, *Phys. Rev.* 160 (1967) 712.
- [22] A.C. Damask, G.J. Dines, *Point Defects in Metals*, Gordon and Breach, New York, 1963.
- [23] J.M. Bolton, B. Henderson, D.O. O'Connell, *Solid State Commun.* 38 (1981) 287.
- [24] E.A. Kotomin, A.I. Popov, *Nucl. Instr. Meth. B* 141 (1998) 1.
- [25] M.A. Monge, R. González, A.I. Popov, R. Pareja, Y. Chen, E.A. Kotomin, M.M. Kuklja, *Defects and Diffusion Forum* 1 (1999) 169–170.
- [26] M.A. Monge, A.I. Popov, C. Ballesteros, R. González, Y. Chen, E.A. Kotomin, *Phys. Rev. B* 62 (2001) 9299.