



**HAL**  
open science

# POINT DEFECTS IN OXIDES. REDUCTION OF IMPURITY IONS IN MgO BY CURRENT FLOW AT HIGH TEMPERATURE

R. Weeks, E. Sonder, J. Pigg, K. Kelton

► **To cite this version:**

R. Weeks, E. Sonder, J. Pigg, K. Kelton. POINT DEFECTS IN OXIDES. REDUCTION OF IMPURITY IONS IN MgO BY CURRENT FLOW AT HIGH TEMPERATURE. *Journal de Physique Colloques*, 1976, 37 (C7), pp.C7-411-C7-414. 10.1051/jphyscol:1976794 . jpa-00216954

**HAL Id: jpa-00216954**

**<https://hal.science/jpa-00216954>**

Submitted on 4 Feb 2008

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

## REDUCTION OF IMPURITY IONS IN MgO BY CURRENT FLOW AT HIGH TEMPERATURE (\*)

R. A. WEEKS, E. SONDER, J. C. PIGG and K. F. KELTON

Solid State Division, Oak Ridge National Laboratory, Oak Ridge,  
Tennessee 37830, U. S. A.

**Résumé.** — Nous rapportons les résultats d'une étude de la réduction par passage d'un courant électrique d'ions de métaux de transition situés en impuretés dans MgO. Les champs utilisés ont été de l'ordre de  $10^3$  V/cm à des températures entre 950 et 1 150 °C. On a pu réduire presque complètement les impuretés bivalentes  $Fe^{3+}$  et  $Cr^{3+}$ , alors que le  $Mn^{2+}$  divalent a été peu affecté. Du  $V^{2+}$  est apparu à la suite du traitement ; il devait vraisemblablement se trouver à l'état  $3^+$  dans le MgO initial.

Les résultats indiquent de plus que le processus de réduction n'est pas uniforme dans les échantillons, qu'il peut être renversé par chauffage en l'absence de champ électrique, et qu'il est accompagné par la création de défauts qui agissent comme des pièges à électrons peu profonds à la température ambiante.

**Abstract.** — Results of a study of the reduction of transition metal impurity ions in MgO due to passage of electric current are reported. Fields of the order of  $10^3$  V/cm and temperatures between 950 and 1 150 °C were used. Trivalent impurities,  $Fe^{3+}$  and  $Cr^{3+}$  could be almost completely reduced, whereas divalent  $Mn^{2+}$  was not greatly changed.  $V^{2+}$  appeared after treatment ; presumably vanadium had been in the  $3^+$  state in the original MgO. The results further indicate that the reduction process is not uniform throughout the samples, that it can be reversed by heating in the absence of an electric field, and that it is accompanied by the creation of defects that act as shallow electron trapping sites at room temperature.

**1. Introduction.** — In ionic compounds, impurity ions can exist in a variety of charge or valence states. Since different impurity charge states affect a variety of crystal properties (for example : optical absorption, electrical conductivity, and mechanical strength), it is of some practical interest to study the mechanisms by which the valence states of impurities change in ionic crystals. Moreover, the processes involved in charge compensation by defects and other impurities are not yet understood in detail, and it is of basic interest to study these mechanisms.

A number of investigators have noticed that the passage of dc current through oxide crystals produces changes in the valence state of some impurities [1]. In order to elucidate the effect of electric current on the charge state of impurity ions, we have performed a number of experiments with MgO containing of the order of 100 ppm transition metal impurities.

**2. Experimental techniques.** — **2.1 SAMPLES.** — Most of the samples used came from two large, irregularly-shaped single crystals of MgO, obtained a few years ago from the Norton Company. These crystals had a slight yellow tint, and analysis of a number of

fragments of both crystals indicated that Fe was the dominant impurity, present to approximately 130 ppm. Table I indicates the amount of Fe, as well as other impurities, detected by semiquantitative spectrochemical analysis.

TABLE I

*Impurities in MgO single crystals  
(parts per million by weight)*

Al	Ca	Cr	Cu	Fe	Mn	Ni	Si	Zr
10	65	15	8	130	10	20	10	30

**2.2 MEASUREMENTS.** — The most useful measurement technique for our purposes was electron paramagnetic resonance absorption, by which the concentration of  $Fe^{3+}$ ,  $Mn^{2+}$ ,  $Cr^{3+}$ , and  $V^{2+}$  could be measured to a relative accuracy of  $\pm 30$  %. Optical absorption measurements were also utilized to probe the  $Fe^{3+}$  and, in some cases,  $Fe^{2+}$  concentrations. Visual changes in some of the samples were also noted, as was an increase in strain that was observed when the samples were viewed through crossed polarizers.

**2.3 SAMPLE TREATMENT.** — All samples were treated in air in a tube furnace at temperatures between 950 and 1 250 °C. The primary experiments were performed

(\*) Research sponsored by the Energy Research and Development Administration under contract with Union Carbide Corporation.

with cubical samples,  $\sim 1$  cm on an edge, that had Pt electrodes either painted (Englehard Pt paste # 6 082) or vacuum deposited on two opposite faces. Electric fields of 1 000 V/cm were used for various times at various temperatures, with the voltage remaining applied while the samples cooled in the furnace. Subsequent to these treatments, which resulted in reduction of many of the impurities, the cubes were sectioned for optical and paramagnetic resonance measurements.

Reoxidation was also studied following reduction treatments. Since it appeared that reoxidation occurred very much slower at a given temperature than reduction, 0.1 cm-thick slices cut from reduced cubes were used for these studies. The reoxidations were performed in air in the same furnace, or one similar to that used for reduction, but without the presence of an electric field.

**3. Results.** — **3.1 SPECIES OF IMPURITIES THAT ARE REDUCED.** — The difference in the paramagnetic resonance spectra depicted in *a* and *b* of figure 1, is

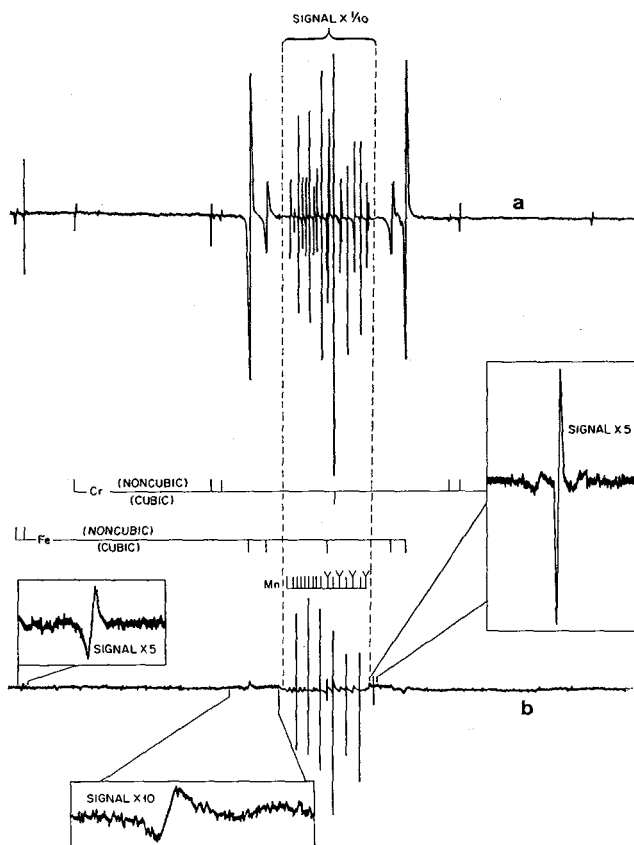


FIG. 1. — Electron paramagnetic resonance spectra of a MgO single crystal measured at 9 GHz at room temperature. *a*) Spectrum of a crystal sample adjacent to specimen treated in an electric field. The signal gain for the central region of the spectrum is reduced by an order of magnitude. *b*) Spectrum of a sample cut from treated crystal ( $\sim 1\ 100^\circ\text{C}$  for 100 h with  $1\ 000\ \text{V}/\text{cm}^{-1}$  applied). The signal gain for the central region of the spectrum is reduced by an order of magnitude. Insets shown are expanded regions of curve (*b*) obtained with greater gain and slower sweep speed.

indicative of substantial reduction of three species of impurities (Fe, Cr, V) and of little change in a third species (Mn). The spectrum in *1a* was obtained on an untreated sample; that in figure *1b* was obtained from a cube that had been treated at  $1\ 100^\circ\text{C}$  for  $\sim 100$  h with a field of 1 000 V/cm. The positions of the well-known absorption lines [2] for  $\text{Fe}^{3+}$ ,  $\text{Cr}^{3+}$ , and  $\text{Mn}^{2+}$  are indicated between the two curves. The most obvious difference between the two curves is the disappearance or large decrease of absorption lines due to  $\text{Cr}^{3+}$  and  $\text{Fe}^{3+}$ , in both cubic and noncubic sites. The insets at the left of figure *1b* show some of the remaining lines measured at greater amplifications and slower scan rates; from such spectra we have estimated that the reduction treatment has caused a concentration decrease of a factor of 20 in the cubic  $\text{Fe}^{3+}$  and a factor of about 8 in the orthorhombic  $\text{Fe}^{3+}$ . Similarly, the  $\text{Cr}^{3+}$  concentration has decreased by more than an order of magnitude. Note that the determination of concentration requires slow scans, such as those depicted in the insets, in order to permit measurement of linewidths. This is necessary because the reduction treatment causes many of the lines to broaden.

The inset at the right is a slow scan at increased sensitivity over the region where the highest field line of the set of 8 ( $M_s = 1/2 \leftrightarrow M_s = -1/2$ )  $\text{V}^{2+}$  hyperfine lines appears. As can be seen in figure *1b*, this highest field line is the only one that is well resolved from the central region where the numerous intense  $\text{Mn}^{2+}$  lines appear and where the gains used to obtain the data for figure *1a* and *b* were reduced by a factor of ten. The  $M_s = \pm 1/2 - M_s = \pm 3/2$  transitions are also evident in the inset on both sides of the  $M_s = +1/2 - M_s = -1/2$  transition. No lines due to  $\text{V}^{2+}$  were detected in any of the unreduced samples. Thus the appearance of this line in the reduced sample indicated that vanadium was originally either aggregated or in the 3+ state, and was respectively either dispersed or reduced from the 3+ to the 2+ state by the treatment. In view of the reduction of Fe and Cr, reduction is the more probably process.

In contrast to the behavior of ions that are originally in the 3+ state,  $\text{Mn}^{2+}$  does not appear to be appreciably reduced by the electrolysis treatment. The ( $M_s = 1/2 \leftrightarrow M_s = -1/2$ ) transitions, for which the change in line width is small, can be seen in figures *1a* and *1b* to decrease by only about 30%. Whether this decrease is significant is difficult to determine from our measurements, since we have observed that impurities in these MgO samples are not always distributed uniformly, and this non-uniform distribution may have given rise to different  $\text{Mn}^{2+}$  concentrations in samples used for obtaining the data of figures *1a* and *1b*. Reduction treatments are performed on 1-cm cubes, which are subsequently sectioned; therefore, it is not possible to perform pre- and postelectrolysis EPR measurements on identical chips.

Comparison of the central parts of the spectra shown, respectively, in figures *1a* and *1b*, appears to

indicate a large difference in amplitude of certain  $Mn^{2+}$  absorption lines. This occurs for transitions

$$(M_s = \pm 3/2 \leftrightarrow M_s = \pm 1/2)$$

and

$$(M_s = \pm 5/2 \leftrightarrow \pm 3/2).$$

However, it is accompanied by a broadening of the originally very narrow Mn lines, such that the total absorption area is not significantly changed. The broadening of transitions other than  $1/2$  to  $1/2$  is also present for the case of the  $Fe^{3+}$  and  $Cr^{3+}$  lines and appears to result from strains within the samples.

**3.2 UNIFORMITY OF REDUCTION.** — An experimental determination of whether reduction proceeds from the anode, from the cathode, or uniformly throughout a crystal would have been useful in identifying the mobile entity involved in the reduction process. We hoped that electrolytic reduction of a number of cubes from the same large ingot as a function of time and temperature, and subsequent sectioning would accomplish that purpose. However, our experiments did not yield the expected results, but rather were indicative

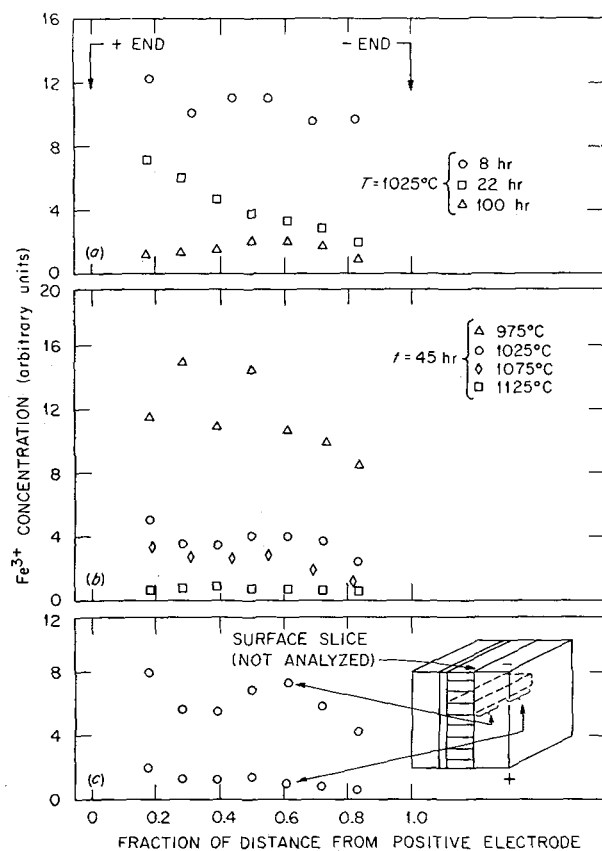


FIG. 2. — Intensities of the  $[M_s = 3/2 \leftrightarrow M_s = 1/2]$  transition in the EPR spectrum of octahedral  $Fe^{3+}$  samples cut from treated MgO crystals. a) Variation of  $Fe^{3+}$  concentration vs position in original cube for different times at a particular temperature. b) Variation of  $Fe^{3+}$  concentration vs position for different temperatures for constant time. c) The intensity as a function of position parallel and perpendicular to applied electric field. The inset depicts positions of slices as cut from an electrolytically treated cube.

of non-uniform reduction. For example, one sample that had been treated at  $1025^\circ C$  for 22 hours exhibited a large gradient in  $Fe^{3+}$  concentration, which suggested that the reduction proceeded from the cathode towards the anode. However, in other samples treated for either shorter or longer times or at different temperatures, only small gradients parallel to the direction of current flow were observed. Figure 2 shows profiles of  $Fe^{3+}$  concentration parallel to the current direction (a) after treatment for different times and (b) for different temperature. The degree of reduction appears to be somewhat greater near the cathode in all these samples, but there is not clear evidence that any reduction front moves through the cubes as a function of time.

To add to the complexity, our measurements indicate that the reduction produces (or increases)  $Fe^{3+}$  concentration gradients perpendicular to the electrolysis field direction. Figure 2c shows two profiles obtained by placing the same samples in the EPR cavity in such a way that the microwave field maximum was near the opposite ends of the samples. Since the samples were cut perpendicular to the original electrolyzing current direction (see inset in figure 2c), these results demonstrate a factor of three difference in  $Fe^{3+}$  concentration in a direction perpendicular to the electrolyzing current. These gradients were verified by scanning optical samples cut from the treated cubes and observing the relative heights of the remaining 280 nm  $Fe^{3+}$  charge-transfer band [3] as a function of position across the samples.

In a number of samples that had been treated at or above  $1125^\circ C$  for periods approaching 100 h, dark streaks connecting the two electrodes became visible. Measurement of the  $Fe^{3+}$  gradient perpendicular to the streak direction indicated a greater reduction of Fe near a streak than in portions of the sample far from the streak. Another observation may be related to the formation of these dark streaks. We repeatedly noticed a current increase in samples that had been undergoing electric-field-induced reduction treatments for long times ( $\sim 100$  h). Such samples exhibited highly non-linear current voltage characteristics, suggestive of electrical breakdown at fields of less than 2000 V/cm. As the temperature of these samples was decreased, progressively higher electric fields were required to produce breakdown.

**3.3 OTHER EFFECTS OF ELECTROLYSIS.** — If samples that have undergone electrolytic reduction are irradiated at room temperature with gamma rays for a short time (15 min in a  $10^6$  rad  $^{60}Co$  source), about half of the reduced Fe is temporarily returned to the  $Fe^{3+}$  state. At room temperature, this  $Fe^{3+}$  concentration decays in about a day; visible light bleaching accelerates the decay of the radiation-produced  $Fe^{3+}$  so that it lasts only a few minutes in strong light (tungsten lamp of spectrophotometer focused on sample). It should be emphasized that this temporary reoxidation of Fe back to  $Fe^{3+}$  occurs only in samples

that have been reduced. In unreduced samples, there is no increase in the  $\text{Fe}^{3+}$  concentration upon a similar gamma irradiation, even though about 30 % of the Fe contained in these samples is originally in the  $\text{Fe}^{2+}$  state. This fact is known both from measurements of the total iron content and from measurement, at liquid-He temperature, of the intensity of the  $\text{Fe}^{2+}$  magnetic dipole zero phonon line [4] at 1 070 nm. In addition, irradiation of reduced samples produces  $\text{V}^-$  centers (or related vacancy defects absorbing at 2.3 eV) [5], which also are unstable and disappear upon either bleaching or room-temperature annealing. These centers also cannot be produced by irradiation of samples that have not first been reduced electrolytically. From the assumption that  $\text{Fe}^{3+}$  is reduced to  $\text{Fe}^{2+}$  by the electrolysis treatment, it follows that the return to the 3+ state is due to the reaction  $\text{Fe}^{2+} + h\nu \rightarrow \text{Fe}^{3+} + e^-$  (trapped). Hence, one is led to conclude that the electrolytic-reduction treatment causes the production of shallow electron traps that are not present in untreated MgO. These traps store electrons, enabling the  $\text{Fe}^{3+}$  concentration to increase, and a small  $\text{V}^-$  (or related defect) concentration to appear via the reaction  $\text{V}^{--} + h\nu \rightarrow \text{V}^- + e^-$  (trapped).

3.4 REOXIDATION AT HIGH TEMPERATURE. — Heating a thin slice from an electrolytically reduced cube

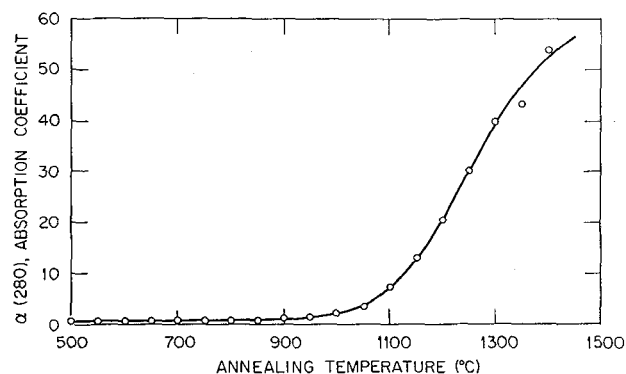


FIG. 3. — The effect of one-hour anneals on a slice from a treated crystal on the absorption coefficient at 280 nm.

will cause reoxidation of the Fe and other impurities so that the sample essentially returns to its original condition. The onset of reoxidation for one of our anneals is  $\sim 1\,000\text{ }^\circ\text{C}$ , as is indicated in figure 3, where data for isochronal anneals of a  $0.05 \times 0.3 \times 0.4\text{ cm}$  slice are shown. To obtain these data, the slice was inserted rapidly into the furnace, held at temperature for 1 h, and quickly cooled to room temperature; then the optical absorption of the  $\text{Fe}^{3+}$  charge-transfer band at 280 nm was measured. Similar results were obtained from EPR measurements.

4. Summary and conclusions. — Our investigations have shown so far that at temperatures above  $1\,000\text{ }^\circ\text{C}$  (which is the range where some impurities in thin slices of MgO can be reduced and oxidized by ambient gases) [1] electric currents cause reduction of a number of trivalent impurities throughout large samples. These electronic treatments can produce essentially complete disappearance of  $\text{Fe}^{3+}$  and  $\text{Cr}^{3+}$ . On the other hand, as the  $\text{Mn}^{2+}$  data indicate, passage of electric current does not as easily cause a reduction of the divalent impurity state.

Measurements on samples taken from different parts of a reduced sample show that reduction due to electric currents does not proceed uniformly throughout a large sample, that it is accompanied by the creation of strained regions and that so-far-unidentified shallow electron traps are created. Our observations also indicate that the high-temperature breakdown strength of MgO is adversely affected by such radiolysis treatments.

The reduced state achieved by electric currents is stable to temperatures above  $1\,000\text{ }^\circ\text{C}$ , indicating that it involves not simply electron transfer, but rather is stabilized by a change in defect structure, stoichiometry or charge compensation that requires defect motion to reverse.

Acknowledgment. — We thank the Norton Company for supplying the crystals used in these experiments.

#### References

- [1] HARWOOD, M. G., Electrical Conductivity of Rutile, III and IV in *Special Ceramics 1964*, p. 199, ed. by P. Popper (Academic Press, New York) 1965.
- [2] HANSLER, R. L. and SEGELKEN, W. G., *J. Phys. & Chem. Solids* **13** (1960) 124.
- [3] HENDERSON, B. and WERTZ, J. E., *Adv. Phys.* **17** (1968) 786.
- [4] SOSHEA, R. W., DEKKER, A. J. and STURTZ, J. P., *J. Phys. & Chem. Solids* **5** (1958) 23.
- [5] HJORTSBERG, A., VALLIN, J. T. and HAM, F. S., *Bull. Am. Phys. Soc.* **21** (1976) 421; HJORTSBERG, A., thesis, Chalmers University of Technology, Goeteborg, Sweden (1975).
- [6] CHEN, Y. and SIBLEY, W. A., *Phys. Rev.* **154** (1967) 842.