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# Dependence of electron and photon emission during abrasion by surface condition of magnesium oxide crystal

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**Abstract**

We measured the simultaneous, time-resolved spectra of photon emission, electron emission, and frictional force during the abrasion single crystal MgO with a diamond stylus in vacuum. phE and EE signal can be detected with millisecond resolution during the wear of a single crystal MgO substrate with a diamond stylus. The emissions and wear behavior are strong function of surface condition, load and stylus velocity. Measurement on annealed vs as-received material show that the luminescence is primarily due to deformation, and the electron emission is primarily due to fracture. These emissions provide insight into the processes responsible for catastrophic failure of ceramics in wear applications.

## 1. Introduction

when a stylus made of hard material is drawn across a soft substrate, the substrate can respond by deforming elastically, plastically or catastrophically by crack growth. the onset of substrate fracture typically produces a dramatic rise in the coefficient friction and terminates the useful substrate life in tribological applications. Although the coefficient of friction is a key property in tribological applications, friction measurement often yield little insight into the evolution of the surface immediately preceding failure. To understand the processes leading up to failure, other probes of the wear process are usually necessary, e.g., microscopic examination of the wear track. However, there observations are difficult to make in real time during the course of a wear experiment. In the case of MgO deformation and fracture produce readily measurable photon emission(phE) [1,2] and electron emission(EE) which, like the coefficient of friction, can be measured in a time-resolved fashion during the wear process. We suggest that these emissions provide useful information on the evolution of MgO substrates during wear, and may shed light on the sequence of events which ultimately lead to ultimate failure.

MgO is a model material for wear studies [3-7], largely because of its simple crystal structure and the availability of single crystal material. MgO also displays limited plasticity and significant work hardening at stresses well below those required for fracture. This property greatly simplifies the study of the deformation processes which ultimately lead to fracture. Although analogous processes are important in more brittle ceramics(e.g., TiC), the small difference between the yield and fracture stresses make it difficult to study the role of deformation in promoting the onset of failure. In this work we show that phE stimulated by deformation processes in MgO can provide time resolved information on the course of plastic deformation during failure —with at least ms resolution. In contrast, the exposure of freshly formed MgO surfaces to the outside world strongly enhances the EE intensities, which thus mark the onset of localized catastrophic failure.

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## 2. Experiment

A diagram of the apparatus for simultaneous phE, EE, and fracture measurements is shown in Fig. 1. As electron multipliers required vacuum conditions, the experiments were in a vacuum system maintained at pressures below $1\times10^{-4}$ Pa. We point out that photon emission measurements do not require vacuum and allow for a great deal more flexibility in the experimental arrangement. Electron emission was detected with a Channeltron Electron multiplier(CEM), Galileo Electro-optics Model 4039 mounted near the substrate. the front cone of the substrate. the front cone of the CEM was biased at +1000 V to attract and efficiently detect electrons. Photon emission was detected with a EMI Gencom 9924QB photomultiplier tube with a fused silica window; this tube is sensitive to 180-600 nm photons, with peak sensitivity in the blue and near UV region of the spectrum. The photomultiplier tube viewed the sample from below, through the MgO substrate and a PMMA sample mount. To provide high sensitivity, the electron multiplier and the photomultiplier were operated in the pulse-counting regime; the outputs were amplified, discriminated, and counted with standard nuclear physics instrumentation.

Single crystal MgO substrates ($2\times2\times0.3$ $cm^2$) were cleaved from a block from Tateho Chemical Industries, Ltd. Cleavage was performed on a stainless steel anvil by aligning a razor blade along a (001) cleavage plane

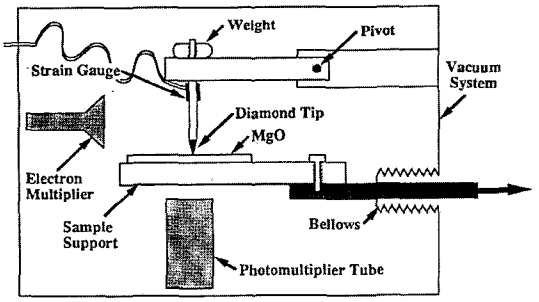


Fig. 1 Diagram of the apparatus employed for simultaneous phE, EE, and frictional force measurements in vacuum.

of the sample and gently tapping the blade with a small hammer. The resulting surfaces were characterized by high densities the of cleavage steps. To provide smoother surfaces for testing, some samples were polished to a 0.25-$\mu m$ finish with diamond paste. some of the polished samples were annealed at 1400℃ for two hours and rapidly cooled(10℃/min) to provide smooth material with a lower yield stress. Abrasion was performed with a commercial diamond scribe(nominal radius of curvature about 100 $\mu m$) mounted in a pivoted cantilever which allowed for the application of a know load. By moving the sample mount at a constant velocity, abrasion could be performed without moving point of contact relative to the detectors. This arrangement allowed for a high, constant photon collection efficiency, and a good electron collection efficiency throughout the experiment. All of the time-resolved measurements described below involved single passes of the scribe over fresh, previously untested portions of the substrate.

The frictional force was estimated by measuring the strain at the end of the aluminum rod with foil strain gauges. This proved to be especially valuable in correlating fluctuations in the frictional force(e.g., produced as the stylus passed over cleavage steps) with the observed emissions. From the gauge specifications and the geometry of the mount for the diamond stylus, we estimate the gauge output to be 190 $\mu V/N$ frictional force. The output of the strain gauge resistance network was amplified with a DC differential amplifier and digitized with a LeCroy 6810 digital waveform analyzer. The results are reported in terms of the strain gauge output.

Measurements of the phE spectrum were made with Thermo Jarrel Ash Monospec-18 Spectrometer(grating 600 lines/nm) equipped with an EG&G Model 1421 gated, intensified, position sensitive detector, sensitive to 200-830 nm photons. Spectral data were acquired with an EG&G OMA-III system. To provide the relatively high phE intensities required for spectra acquisition, the diamond scribe was repeatedly drawn back and across an MgO substrate mounted on the entrance slit of the spectrometer.

## 3. Results

Nakayama and Hashimoto have measured the photon and charged-particle emission during the abrasion of $Si_3N_4$, $Al_2O_3$, and $ZrO_2$ with a diamond stylus in a variety of atmospheres they attributed the observed emissions to gaseous discharges accompanying contact charging and dielectric breakdown of the ambient gas. [2,3] This does not appear to be true for MgO, at least in the case of phE. Fig. 2 show that a wear track of MgO surface with high densities of cleavage steps. The emission spectra and the frictional force were strongly dependent on the surface condition. A phE spectrum generated during abrasion of single crystal MgO with a diamond stylus in air is shown in Fig. 3. The spectrum is characterized by three emission bands at about 710 nm, 520 nm, and 420 nm, respectively, and a broad shoulder into the UV. The absence of $N_2$ spectral lines is inconsistent with gaseous discharge in air. In contrast to materials systems such as diamond on $Al_2O_3$ the phE due to diamond on MgO is not due to electrostatic breakdown of air, rather, phE is produced by the electronic excitation of defects in the solid phase. The observed spectrum is described further in the discussion.

The yield stress of MgO, and consequently the wear behavior, can be significantly lowered by annealing treatments. At modest load and low stylus velocities, deformation and fracture are competing mechanisms for energy dissipation. Thus lowering the yield stress will enhance plastic deformation and reduce the amount of fracture. Emission measurements were made on polished (not annealed) and polished-annealed MgO as a function of stylus velocity. The total number of phE and EE counts recorded during the production of a 1.5-cm wear track are shown in Fig. 4. At stylus velocities below about 0.3 cm/s, the emissions from polished and polished-annealed samples both increase rapidly with increasing stylus velocity. In this range of velocities, the annealing treatment lowers the EE intensities an order of magnitude and raises the phE intensities almost a factor of two. This is consistent with the expectation that phE is largely due to plastic deformation processes, while EE is associated with fracture.

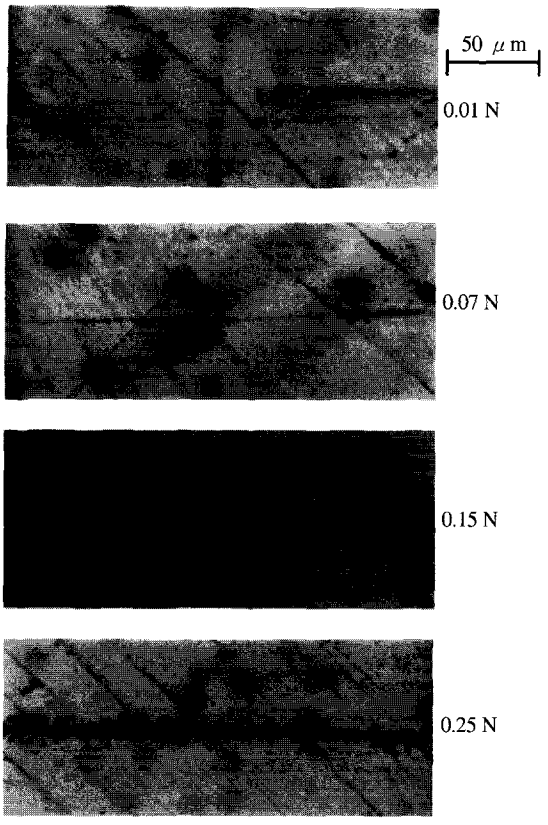


Fig. 2 Optical microscope images of a wear track of MgO surface with high densities of cleavage steps.

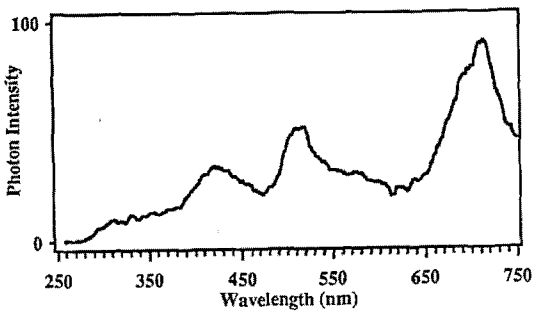


Fig. 3 phE spectrum produced by repeated passes of a diamond stylus over an MgO substrate.

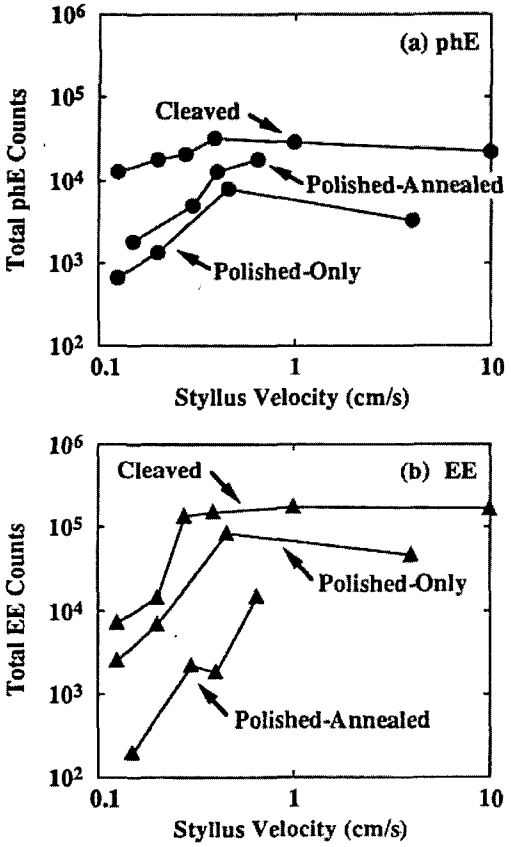


Fig. 4 Total phE and EE count detected during the formation of a 1.5 cm wear track as a function of stylus velocity for cleaved, polished, and polished-annealed MgO. In each case, the stylus was loaded with a 10 g mass.

## 4. Discussion

### 4.1 phE Spectra

The major features of the phE spectrum during repeated abrasion can be readily interpreted in terms of previously observed excitations in MgO. the red, 710-nm band is characteristic of impurity $Cr^{3+}$(the $Cr^{3+}$ R line), [11] with sidebands at longer and shorter wavelengths due to vibrational. The green, 520-nm band has been assigned to the decay of excited F-centers [12](oxygen vacancies containing two electrons). Significantly, emission in this region has not been observed in the photoluminescence(PL) or cathodoluminescence(CL) spectra of previously deformed MgO. The principal feature in the PL and CL spectra of deformed MgO is the blue, 420-nm band. [13,14] This deformation-related band is similar to the PL peak due to isolated $F^+$-centers(centered at 410 nm). [12] The 420-nm band in deformed material appears to be a composite peak due to emission from oxygen vacancies and vacancy clusters. [13,14]

The short wavelength tail PL spectrum of Fig. 3 is especially intriguing as it requires the production of rather energetic excitations(> 4 eV). MgO CL spectra often show a peak in the 235-250 nm region, [15-18] which is attributed to electron tunneling from electron traps(e.g, F and $F^+$ centers) to magnesium vacancies(V- and $V^-$-centers). $Fe^{3+}$ impurities in the MgO employed in this work absorb strongly at wavelengthes below 260 nm and would account for the lack of a definite peak at shorter wavelengths.

We note that the photomultiplier tube employed in the pulse counting work does not respond to wavelengths below 600 nm. Thus the $Cr^{3+}$ excitation would contribute little to time-resolved phE signals described above. The quantum efficiency of the photomultiplier tube employed in this work peaks in the blue near UV. Therefore, photons produced by the decay of excited $F^{3+}$-centers (420-nm band) would be detected with especially high efficiencies.

### 4.2 Emission mechanism

The mechanism for phE stimu- lated by deformation is not known. It is clear that high densities of point defects are produced by deformation in MgO and the alkali halides, presumably by a jog dragging mechanism. Jogs formed at the intersection of moving dislocationts impede) but do not necessarily stop) further dislocation motion. Crystallographic constrains require that a trail of vacancy pairs(or interstitial pairs) be produced when a screw dislocation "drags" a jog through the lattice. The relatively high energy required for interstitial formation strongly favors the formation of vacancy defects. Thus

dislocation motion in the presence of high dislocation densities can produce high densities if vacancy defects.

Williams and Turner suggest that charge exchange between point defects and moving dislocations can excite point defects. There is some evidence that the conduction band along an edge dislocation is a couple eV below the normal conductions band. [19] If the F-center and $F^+$- center energies lie high in the band gap, as suggested by Gibson et al., [20] moving dislocations could steal electrons from nearby F-type centers. This is not likely to be a radiative transition, however. The best available evidence suggests that the characteristic 520-nm and 420-nm emissions are produced when conduction band electrons are captured at F`-and $F^+$centers to form excited $F^+$-and F`centers, respectively. In this case, deformation elevates electrons all the way to the conduction band. One possibility is that electron traps(oxygen vacancies) are temporarily annihilated by moving edge dislocation. An edge dislocation locally looks like a row of interstitials, and individual ions along the dislocation would be vulnerable to "recombination" with appropriate vacancies. The transient annihilation of oxygen vacancies by an $O^{2-}$-ion would render any electron trapped at the vacancy extremely unstable, and in the absence of nearby unfilled electron traps could promote them to the conduction band. Subsequent retrapping of conduction band electrons at oxygen vacancies or vacancy clusters would then produce the observed emissions.

Both phE and EE are observed when MgO is fracture in vacuum, presumably due to the recombination of charge carriers at appropriate traps. Again, the mechanism for the formation of excited states is not clear. It is possible that much of the emission, both phE and EE, is ultimately deformation related. In the present work, the majority of the phE appears to be due to deformation. This is partly a consequence of the high volume of deformed material produced by abrasion, but it may also reflect what we expert to be relatively low crack velocities during wear-related fracture. phE and EE intensities during fracture tend to be strong functions of crack velocity. [21]

## 5. Conclusions

Significant phE and EE signals can be detected with millisecond resolution during the wear of a single crystal MgO substrate with a diamond stylus. The emissions and wear behavior are strong function of surface condition, load, and stylus velocity. In particular. the phE appears to be sensitive to deformation processes in the bulk, as suggested by the increase in phE intensities produced by annealing the MgO. Conversely, the surface-sensitive nature of EE, its strong dependence on stylus velocity, and the depressed EE intensities from annealed material are all consistent with EE due to localized fracture.

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