Effect of Oxygen Vacancies on the Mechanoluminescence Response of Magnesium Oxide

Ekaterina Novitskaya, Aaron Manheim, Manuel Herrera*, and Olivia A. Graeve*

ABSTRACT: The mechanoluminescence response of oxide materials has implications for the use of these materials in structural health monitoring applications, where crack propagation needs to be monitored. Thus, we describe the mechanoluminescence of MgO powders, showing that the signal is dependent on the existence of oxygen vacancies. Cathodoluminescence (CL) spectra of the powders exhibited an emission at 2.10 eV associated with F^+ centers (oxygen vacancies), as well as intense CL emissions at 3.70 and 4.10 eV, associated with M^+ and M^- centers (paired-oxygen vacancies). Furthermore, CL measurements revealed an emission at 1.70 eV, which was not influenced by mechanical stress, and can be attributed to an electronic transition between excited and ground F^+ states. The presence of oxygen vacancies was confirmed by X-ray photoelectron spectroscopy and electron energy loss spectroscopy. Measurements of CL intensity with respect to electron irradiation time confirmed the presence of high amounts of F^+ centers, as well as a saturation time effect, in which emission intensity achieves a maximum only after a certain time of irradiation. The existence of this saturation effect was correlated to the mechanoluminescence signal.

Keywords: Mechanoluminescence; magnesium oxide; oxygen vacancy; cathodoluminescence; F-center; M-center

1. INTRODUCTION

Mechanoluminescence is a unique light-emitting phenomenon activated by deformation or fracture of a material.¹⁻² The mechanisms responsible for mechanoluminescence are not completely understood, but current models suggest that a material's fracture results in an electrical polarization, which causes an electric discharge that ionizes the surrounding air and results in a flash of light.³ Bright mechanoluminescence emissions have been reported in a variety of materials, including MgSO4•*x*H₂O and ZnSO4•7H₂O, cholesteryl salicylate crystals,⁴ and europium tetrakis (dibenzoylmethide) triethylammonium.⁵ There are two main sub-types of mechanoluminescence.⁶ The first category consists of deformation mechanoluminescence, which includes elastic-, plastic-, and fracture-mechanoluminescence, based on the stage in the stressstrain response of the material at which luminescence occurs. The second category consists of electrically-, thermally-, and chemically-induced mechanoluminescence, with the classification made according to the nature of the force which activates the corresponding luminescence response.

There are some additional sub-classifications of these two main mechanoluminescence categories.⁷ For example, plastic-mechanoluminescence is divided into four sub-categories, including dislocation mechanical interaction-induced luminescence, dislocation electrostatic interaction-induced luminescence, charged dislocation electrification-induced luminescence, and thermal excitation-induced luminescence. For a specific example of these phenomena, one can explore the main mechanism behind the dislocation interaction-induced plastic mechanoluminescence. The process is the result of a mechanical interaction between dislocations and defect centers in a process of transfer of electrons from defect centers to the dislocations. Subsequent movement of dislocations transfers electrons to the recombination centers, producing a luminescence signal. X-ray irradiated alkali halide crystals produce this type of mechanoluminescence.⁷ Another type of plastic-mechanoluminescence, produced by electrostatic interactions between the charged dislocations and defect centers, is called dislocation electrostatic interaction-induced mechanoluminescence. Here, luminescence is produced by the movement of electrons from defect centers into the conduction band with their subsequent recombination. The luminescence produced in impurity-doped II-VI compounds, say ZnS:Cu, is a good example of this type of phenomenon.⁸ Charged dislocation electrification-induced by strong electric fields due to the glide of charged dislocations onto the crystal surface during deformation. This dislocation glide causes luminescent flashes due to surface breakage. The luminescence observed during plastic deformation of II-VI crystals such as ZnS has been ascribed to this phenomenon.⁹

The mechanoluminescence response from MgO has been attributed to thermallyactivated electronic transitions in areas of high stress of the crystal.³ This type of thermal excitation-induced mechanoluminescence has also been seen in LiF, NaF, and NaCl.¹⁰ Particularly, Langford *et al.*³ studied the mechanisms behind the fracture-emission of singlecrystal MgO (99.99% purity), and this emission has been found to be sensitive to the presence of defects created during crack formation. Since the study was completed on relatively pure MgO single crystals, a systematic determination of the impact of impurity/defect concentrations on the mechanoluminescence response of this material is not available. In addition, it is known that most optical and electronic properties in MgO are due to the presence of a variety of defects, with the most important defects being those created by oxygen vacancies, called *F* centers.¹¹ Also, it has been previously demonstrated that the concentration of *F* centers in MgO can potentially be estimated from the intensity of photoluminescence spectra of the material in the blue/green region of the spectrum.¹²⁻¹³

In this study, the mechanoluminescence response of MgO powders is described with respect to oxygen vacancies present in the material. The strongest mechanoluminescence response was correlated to the existence of oxygen vacancies (*F* centers) and paired-oxygen vacancies (*M* centers), confirmed by X-ray photoelectron spectroscopy, electron energy loss spectroscopy and cathodoluminescence.

2. EXPERIMENTAL METHODS

MgO was synthesized by solution combustion synthesis¹⁴ using magnesium nitrate as oxidizer and carbohydrazide as organic fuel.¹⁵⁻²⁴ The reagents used were magnesium nitrate hexahydrate [Mg(NO₃)₂•6H₂O, 98-102%, Alfa Aesar, Ward Hill, MA] and carbohydrazide [CO(NHNH₂)₂ 97%, Alfa Aesar, Ward Hill, MA]. Fuel to oxidizer ratio was maintained at 0.625 according to stoichiometric reaction calculations.²⁵ A mixture of 31.81 g of Mg(NO₃)₂•6H₂O and 6.99 g of CO(NHNH₂)₂ were dissolved in 100 mL of deionized water. The solution was stirred for 30 minutes. Next, the solution was placed in a muffle furnace at 773 K. After water evaporation, the mixture combusted, and the resulting powders were recovered. A subsequent thermal treatment at 1473 K for 2 hours was performed on the powders immediately after synthesis. These powders will be referred to as MgO(SCS). In addition, five commercially available MgO powders of different purities were characterized. These powders had vendor reported purities of 95%, 96%, 99%, 99.95% and 99.998%, and will be referred to as MgO(1), MgO(2), MgO(3), MgO(4) and MgO(5), respectively. Impurity information for the MgO commercial powders and Mg(NO₃)₂, which was used as precursor for MgO(SCS), are listed in Tables S1 and S2.

The morphology of the powders was analyzed on a FEI-XL30 scanning electron microscope (SEM) [FEI Company, Hillsboro, OR] using a 10 kV accelerating voltage. For SEM imaging, all samples were mounted on aluminum sample holders and sputter-coated with iridium. The powders were also imaged using transmission electron microscopy (TEM) on a G2 Sphera system [FEI Company, Hillsboro, OR] with a 200 keV accelerating voltage. For electron energy loss spectroscopy (EELS) measurements, a JEOL 2100F scanning transmission electron microscope (STEM) was used, operated at 200 keV and equipped with a Gatan spectrometer. Quantification of elements was performed using Digital Micrograph Gatan software, after background removal with a power-law model, by fitting the *K*-edge of detected elements with a Hartree-Slater model.²⁶ The relative sample thickness for the studied region, calculated from the zero-loss signal, was 0.25 times the inelastic mean free path of the electron beam, which represents low scattering processes.²⁷

Phase, crystallite size, and lattice parameters of the powders were characterized by X-ray diffraction (XRD) on a D2 Phaser [Bruker AXS, Madison, WI] using a step size of 0.02 degrees 20 and a count time of 1 s by scanning from 15 to 85 degrees 20. Lattice parameters and crystallite sizes were calculated using Rietveld refinement using TOPAS 4.2 software [Bruker AXS, Madison, WI]. Particle size distributions were determined using a Microtrac [Microtrac Inc., Montgomeryville, PA] Nanotrac ULTRA dynamic light scattering (DLS) [28-37] system by dispersing approximately 25 mg of powder in 25 mL of ethanol, stirring for 15 minutes, and ultrasonicating for 15 minutes. Thermogravimetric (TGA) analysis of the powders was performed on a Q600 instrument [TA Instruments, New Castle, DE] in both air and argon

atmospheres from room temperature to 1773 K using a heating rate of 20 K/min. This instrument has a baseline drift of 50 μ g. Cathodoluminescence (CL) spectra were obtained in the SEM using a Gatan MonoCL4 system at room temperature in the UV-visible spectral range. X-ray photoelectron spectroscopy (XPS) measurements were acquired in a SPECS system equipped with a PHOIBOS WAL analyzer using an Al anode. High-resolution spectra were obtained using 300 scans during the measurement, using windows of 0.1 eV sensitivity. To estimate the areal intensity of O 1*s* and Mg 2*p* components, the final spectra was deconvoluted into Gaussian peaks using a Shirley background with the aid of CasaXPS processing software. The obtained XPS spectra were calibrated using the C 1*s* signal (284.6 eV) as reference. The CL and binding energy intensities were plotted in units of kilocounts per second (kcps).

Mechanoluminescence measurements of the materials were obtained by using a drop tower testing methodology.³⁸ The instrument built for this purpose consisted of a PVC pipe of 1.5 cm inner diameter, drilled on the upper side with a hold for a pin that supported a 1.27 cm diameter steel ball (13.8 g). Upon removal of the pin, the steel ball descended and impacted the sample, which was placed on a steel plate at the bottom of the PVC pipe. The impacted MgO powder transformed into a flake shape MgO ceramic. The steel ball was dropped from a height of 0.905 m to generate the luminescent signal that was recorded by using a fused silica optical fiber attached to a Hamamatsu R928 photomultiplier tube (PMT). The detected panchromatic signal was amplified with a Keithley 2400 current amplifier converting the current signal to a voltage signal and finally captured with a Hantek DSO5102P oscilloscope. Once the signal was collected, ten spectra were recorded from each sample and averaged. To determine the emission wavelength of the mechanoluminescence signal of the MgO(SCS) sample, optical bandpass interference filters (Edmund Optics) with wavelength centers of 385, 394, 430, 500, 550 and 650 nm were placed between the optical fiber and the PMT detector.

3. RESULTS AND DISCUSSION

3.1. Characterization of Oxygen Vacancies

Powder characteristics, including crystallite sizes and lattice parameters determined from XRD, and particle sizes determined from DLS, together with general morphologies determined from SEM, are listed in Table 1. X-ray diffraction patterns of the MgO powders are summarized in Figure 1 and correspond to the cubic phase of MgO (PDF#00-045-0946). Sample MgO(2) also contains a small amount of an unknown secondary phase. The crystallite sizes of the MgO(SCS) powders are in agreement with previously reported data on MgO produced by a similar methodology.³⁹ Furthermore, very small changes in lattice parameters for all the materials are noted (see Table 1), suggesting the absence of significant substitutional impurities in the materials, which can potentially result in lattice parameter variations.⁴⁰⁻⁴¹ The lattice parameter values are in close agreement with those reported by Janet *et al.*¹² for MgO nanopowders produced at different calcination temperatures. The scanning electron micrographs obtained for the MgO(SCS) powders show features common in combustion-synthesized materials, namely porous agglomerates.

In order to explore the presence of volatile impurities in the powders, TGA analysis was performed in air and argon atmospheres and illustrated in Figure 2. Additionally, Table 2 summarizes weight changes of the MgO powders as a result of heating in air and argon atmospheres. Figure 2(a) corresponds to the results for MgO(1) and MgO(SCS), whereas the

results for powders MgO(2), MgO(3), MgO(4), and MgO(5) are plotted for heat treatments in air and argon atmospheres in Figures 2(b) and 2(c), respectively. Results from Figure 2(a) show that MgO(1) loses weight upon heating in both air and argon atmospheres. In contrast, the MgO(SCS) powder gains weight (about 0.8%) during the thermal treatment in air. We interpret this as a recovery of oxygen and concomitant elimination of oxygen vacancies (V₀) present in the MgO powders, as well as concurrent elimination of surface impurities. The incorporation of atmospheric gases in vacancy defects during thermal treatments has been widely reported previously.⁴² Testing of MgO(SCS) in an argon atmosphere reveals that the weight of this material decreases by 2.8 wt.%, which can be attributed to the elimination of surface impurities, commonly found in combustion-synthesized powders.¹⁴

Assuming that the powders annealed in air loss the same amount of surface impurities as the powders annealed in argon, then a simple approximation tells us that recovery of stoichiometry requires an oxygen gain of 3.6 wt.% (2.8 wt.% + 0.8 wt.%). The weight change for the rest of the materials was found to be negative in air and argon atmospheres, indicating very small amounts (or absence) of oxygen vacancies. In fact, the weight loss for MgO(3), MgO(4), and MgO(5) was almost the same for both oxygen and argon atmospheres [see Figures 3(b) and (c) and Table 2], indicating that weight loss is associated with external impurities and not with the recovery of oxygen stoichiometry or any changes internal to the powders. Of note is that the weight loss for the MgO(2) powder is quite significant compared to the MgO(3), MgO(4), and MgO(5). According to the vendor certificate of analysis, the loss on ignition (LOI) for MgO(2) was more that 5%, demonstrating the presence of significant volatile surface impurities in this material. From these results, the notion that there are significant oxygen vacancies in the MgO(SCS) powders is qualitatively demonstrated.

XPS characterization was performed to determine the atomic composition on the surfaces of the MgO(1) and MgO(SCS) samples. Peaks associated with O 1s, Mg 2s, Mg 2p, K 2s, Ca 2s and Ca 2p are present in the spectra (Figure S2). Deconvoluted XPS spectra for the O 1s signal for MgO(1) (Figure 3a) and MgO(SCS) [Figure 3b] show components centered at binding energies of 529.5 eV, 531.5 and 532.1, which match closely with the values reported for the Ca-O, C=O and Mg-O binding energies, respectively.⁴³⁻⁴⁵ The signal for C=O corresponds to adsorbed residual atmospheric gases.⁴⁴ The Ca-O signal shows that the powders contain some CaO, although it is minimal and not detectable by XRD. The Mg 2p and O 1s signals were analyzed by CasaXPS software with a Shirley curve as a background. According to the analysis of the component at 532.1 eV, assigned to the Mg-O binding energy, 79.6 and 82.8% of the signal correspond to oxygen 1s in MgO(1) (Figure 3a) and MgO(SCS) (Figure 3b), respectively. By applying this result to evaluate the composition of the powders, we calculate that the atomic composition of MgO(1) is about 47.9 at.% oxygen and 52.1 at.% magnesium, while for MgO(SCS) it is about 45.8 at.% oxygen and 54.2 at.% magnesium. In either case, the stoichiometry indicates oxygen deficiency in both samples. Figures 3c and 3d show that the Mg 2p signals only have one component with a binding energy of 50.2 eV and 50.3 eV, respectively, corresponding to the Mg-O bond.⁴³

A high-resolution transmission electron micrograph of MgO(SCS) is shown in Figure 4a, with stacking faults along the [100] direction (marked by black arrows). Maoz *et al*.⁴⁶⁻⁴⁷ have observed the formation of this type of defects in MgO nanostructures, where numerous stacking faults occur at the boundaries of slightly misoriented MgO nanocrystals. The formation of stacking faults typically correlates with the formation of point defects, mostly vacancies,⁴⁸⁻⁵¹ particularly oxygen vacancies in MgO, which explains the high deficiency of oxygen found in

the analyzed region shown in Figure 4a. Local EELS measurements obtained in the region shown in Figure 4a resulted in the detection of the *K*-edges for O and Mg, centered at 537.0 eV and 1319.0 eV, respectively, as illustrated in Figure 4b. The quantification of these signals was performed using Digital Micrograph Gatan software by fitting the *K*-edge of detected elements with a Hartree-Slater model, after background removal with a power-law model, revealing an atomic composition for O and Mg of around 34.9 and 65.1 at.%, respectively. Thus, both XPS and EELS results reveal the presence of oxygen deficiency. However, the percent oxygen from each technique do not match because of the extremely localized signal from EELS, whereas the XPS signal represents an average measurement from a larger area.

3.2. Characterization of Luminescence

Mechanoluminescence measurements show that the MgO(SCS) and MgO(1) powders display the highest mechanoluminescence intensities, defined by the maximum recorded voltage of $(3.05 \pm 0.12) \times 10^2$ and $(1.19 \pm 0.10) \times 10^2$ V, respectively, illustrated in Figure 5a and summarized in Table 2. The MgO(SCS) was found to generate the highest mechanoluminescence response among all materials tested, with a response about three times higher compared to the best commercially available material [*i.e.*, MgO(1)]. Other samples exhibited intensities lower than ~10 V (see Figure 5b and Table 2).

To evaluate the fluorescence decay behavior of the mechanoluminescence signals, the experimental spectra were fitted with a Kohlrausch-William-Watts (KWW) function:⁵²

$$I(t) = I_0 e^{-\left(\frac{t}{\tau}\right)^{\beta}}$$
(1)

for values after the peak of the signal, marked by I_{max} and a dashed line in Figure 5a. The onset of decay time corresponds to t = 0.32 ms for MgO(1) and t = 0.45 ms for MgO(SCS). The inset in Figure 5a shows the curve fit redefining time from t to t^* (representing time only for signal decay). The KWW function describes the exponential decay of fluorescence intensity, I(t), which drops to 1/e of its initial value I_0 after the decay time constant, τ , for any value of the stretching exponent β ($0 < \beta \le 1$). This stretching exponent is a measure of the relaxation rates involved in the fluorescence decay process, where a small value means a broader rate distribution. The inset in Figure 5a shows the curves obtained after fitting the mechanoluminescence data to the KWW function with $\beta = 1$, resulting in coefficients of determination, R^2 , of approximate unity,⁵³ specifically 0.9962 for the MgO(SCS) powders and 0.9979 for the MgO(1) powders. The inset in Figure 5a also shows that the obtained decay time constant is 459 µs for MgO(SCS) and 691 µs for MgO(1). Table 2 summarizes the decay times calculated for all samples with values roughly between 500 and 700 µs. Figure S3 shows the decay times calculated for samples MgO(2), MgO(3), MgO(4) and MgO(5).

Figure 6 depicts the cathodoluminescence spectra of all commercial MgO powders, organized in order of decreasing intensity of the 1.70 eV peak. The MgO(1) (Figure 6a), MgO(4) (Figure 6c), MgO(2) (Figure 6d), and MgO(5) (Figure 6e), powders exhibit a broad cathodoluminescence emission centered at 2.95 eV, attributed to the presence of oxygen vacancies,⁵⁴ with a shoulder at about 3.30 eV.⁵⁵ The MgO(3) powder (Figure 6b) exhibits three bands centered at 2.60, 3.30, and 4.90 eV.⁵⁶ The emission of 2.60 eV has not been reported for MgO and we have assigned it to the presence of CaO impurity,⁵⁷ based on the impurity analyses provided by the vendor (see Table S1), where one can see that the MgO(3) powder contains ~0.8 at.% of CaO. This emission is also present in the MgO(1) and MgO(2) powders, which contain

0.1 at.% and 0.83 at.% CaO, respectively. According to Schleicher et al.,55 the emission at 3.30 eV corresponds to the electronic transition between F^{2+} centers (oxygen vacancies without trapped electrons) and the excited states of F^{+*} centers (oxygen vacancies with one trapped electron) in MgO. Furthermore, Figure 6 also reveals the presence of a red band centered at 1.70 eV, which changes in intensity in order of MgO(1) \rightarrow MgO(3) \rightarrow MgO(4) \rightarrow MgO(2) \rightarrow MgO(5), from highest to lowest. This is the same trend observed for the mechanoluminescence intensities summarized in Figure 5. Generally, samples of higher purity have lower mechanoluminescence and cathodoluminescence emission intensities of the 1.70 eV emission, in contrast to the samples of lower purity that have higher emission intensities. That is, the MgO(1) powder exhibits the highest red cathodoluminescence intensity, while the MgO(5) powder exhibits the lowest intensity. As was stated earlier, the MgO(1) powder also displays the highest mechanoluminescence intensity, while the MgO(5) powders displays the lowest (see Figure 5). Zhang et al.⁵⁸ previously reported that MgO nanobelts generate an emission of 1.7 eV by relaxation luminescence of defect centers, excited by a mechanical stress during fracture and crack propagation. In addition, Schleicher et al.55 proposed that the MgO emission at 1.7 eV corresponds to electronic transitions between excited F^{+*} states and ground F^{+} states.

In order to confirm that the 1.70 eV emission in our own powders is generated by mechanical stress, a monochromatic mechanoluminescence measurement of MgO(SCS) was obtained. This monochromatic measurement was performed by using a bandpass interference filter placed at the window of the detector, ensuring only the detection of the luminescence of 1.70 eV. This result showed an estimated decay time of 470 μ s (Figure 7), which is very close to the 459 μ s value evaluated from the panchromatic mechanoluminescence measurement for this sample (see Figure 5a and Table 2). Thus, we demonstrate that mechanical stress in MgO

promotes a generation of the 1.70 eV emission, probably due to electronic transitions from the excited F^{+*} states to the ground F^{+} states.

Figure 8 illustrates the cathodoluminescence spectra of the MgO(SCS) powder obtained before and after impact associated with the mechanoluminescence measurements. Several components centered at 1.70, 2.04, 3.30, 3.70, and 4.10 eV, were calculated by deconvolution operations using Gaussian curves. A decrease in cathodoluminescence after impact is seen when comparing the two spectra. The signal in Figure 8a has an intensity reaching ~ 100 kcps for the peak of highest intensity, whereas the signal in Figure 8b has an intensity no higher than \sim 50 kcps for the same peak. In considering the peaks from the deconvolution, one can see that the signals at 2.04, 3.30, 3.70 and 4.10 eV all decrease in intensity, potentially due to annealing of the point defects that originate these emissions. The annealing process, due to heating of the MgO powders during impact, promotes the diffusion of the point defects from the bulk of the solid to the surface, thus resulting in the annihilation of the defects. In particular, the inelastic collision of the steel ball with the MgO powder during mechanoluminescence testing generates heating by conversion of mechanical energy to thermal energy. An approximation of the maximum temperature achieved, assuming that mechanical energy is converted entirely into heat, results in a value of around 1500 K, considering that the kinetic energy of the steel ball at impact is 0.122 J, the specific heat capacity C_v of MgO is 40 J/mol•K,⁵⁹ and the average mass of the MgO powder exposed to the impact is approximately 1.0×10^{-4} g, an amount that can be justified considering the small contact area of a steel sphere when impacting a flat surface. We propose this high temperature is enough to promote annealing of the defects. SEM images obtained from the MgO(SCS) powders after mechanical impact show sintering between the powder grains (Figure 9c), as compared to the powders before impact (Figure 9a). The

cathodoluminescence emission scan obtained after impact revealed an inhomogeneous emission (Figure 9d), as compared to the emission before impact (Figure 9b), an effect which can be attributed to an inhomogeneous distribution of point defects due to annealing from the impact.

The cathodoluminescence component of 2.04 eV in Figure 8, has been previously associated with the presence of F centers at low-coordinated sites, as steps and corners, in MgO(100).⁶⁰ However, several authors have reported that MgO exhibits luminescence of type F^+ and F⁰ with energies of about 3.2 eV and 2.3 eV, respectively.⁶¹⁻⁶³ Moreover, Rinke et al.⁶⁴ reported that the emissions at 2.3-2.4 eV are generated when electrons in F^0 and F^+ centers recombine with holes in the valence band of MgO. Therefore, we assigned the component of 2.04 eV in our MgO(SCS) sample to the reported emission of about 2.3 eV, associating its origin to the presence of F^+ centers in the sample. Furthermore, the components of 3.70 and 4.10 eV could correspond to the formation of M centers (paired oxygen vacancies), according to Schleicher *et al.*⁵⁵ who have proposed that the energy levels of M centers are located at around 4.3 eV below the conduction band, while the energy between M centers and the valence band is about 3.8 eV. Additionally, Dominguez-Ariza et al.65 used self-consistent methods to determine that the neutral M center exhibits a very intense emission at around 4.4 eV, while the charged M^+ center shows intensities between 3.7 and 4.0 eV. Since the MgO(SCS) powders exhibit high oxygen deficiency, confirmed from the EELS, XPS, and TGA measurements, the formation of M centers is highly probable in this sample. As a result, we attribute the components of 3.70 and 4.10 eV to the electronic transitions between M^+ and M centers, respectively. While all signals discussed above decrease in intensity after impact, Figure 8 shows that the deconvoluted peak at 1.70 eV has an intensity that is approximately the same in both spectra (~9 kcps). This peak has been associated with the presence of F^+ centers in MgO.⁵⁵ The presence of the peak at 1.70 eV,

of the same intensity as that seen before impact, shows that F^+ defects are highly stable in MgO (*i.e.*, they have low free energy).

Furthermore, Figure 10 displays the cathodoluminescence intensity variation with respect to electron-beam exposure time observed for powders under irradiation with a voltage of 15 keV and beam current of 3.2×10^{-13} A/µm². Emission from the MgO(SCS) (Figure 10a) and MgO(1) (Figure 10b) powders display a gradual increase of the CL intensity with beam irradiation until the signal reaches a maximum. The saturation intensities for the MgO(SCS) and MgO(1) samples were 36.8 and 40.9 kcps, respectively, occurring at times of 25 and 180 s. The curves obtained from these two samples revealed an excellent fit using the Monod equation, typically used for modeling systems composed of species that grow in number and are immersed in a limited environment:⁶⁶

$$I_{\rm CL} = I_{\rm sat} \ \frac{t}{b+t} \tag{2}$$

where I_{sat} is the saturation cathodoluminescence intensity, *b* is a constant associated with the intensity rate of increase, and *t* is the beam irradiation time. We propose using the Monod equation to describe the behavior illustrated in Figure 10 by considering MgO as a system composed of a limited number of F^+ centers. Following Jonnard *et al.*⁶⁷, the F^+ centers transform to *F* centers through electron beam irradiation due to the capture of one electron as follows:

$$F^+ + e_i \rightarrow F^{+*} + e_i \tag{3}$$

$$F^{**} \to F^{+} + h\nu \tag{4}$$

$$F^{+*} + e_{\rm th} \to F^* \tag{5}$$

$$F^* \to F + h \mathbf{v}^{\prime} \tag{6}$$

where e_i represents one incident electron from the electron beam, and e_{th} represents one electron from the conduction band. Equations 4 and 6 represent the cathodoluminescence emission generated during the transformation $F^+ \rightarrow F$, which increases with time until a maximum or saturation cathodoluminescence intensity, determined by the amount of F^+ centers available in the MgO samples. Figure 10a shows a considerably higher saturation cathodoluminescence intensity for the MgO(SCS) powder, compared to that observed in Figure 10b for the MgO(1) powder, corresponding with the higher concentration of F^+ centers contained in MgO(SCS). Thus, measurements of cathodoluminescence dependence upon irradiation time confirm the presence of a high density of F^+ centers in MgO(SCS) and MgO(1) samples, and this can be correlated to the signal intensity of mechanoluminescence in the powders, especially when comparing to Figure 10c, which shows that the rest of the powders do not exhibit this CL intensity saturation with time effect. Since we have shown that MgO(2), MgO(3), MgO(4) and MgO(5) do not contain significant oxygen vacancies, we associate the lack of saturation effect in these powders precisely with the lack of oxygen vacancies. This is also connected to the lack of a mechanoluminescence signal.

In summary, an analysis of the mechanoluminescence response of several commercial MgO powders together with MgO produced by a solution combustion synthesis process was performed. The presence of several different types of oxygen vacancies was found to be responsible for the mechanoluminescence signal in MgO. Specifically, F^+ , F^0 , and M centers, verified and characterized by thermogravimetric analysis, X-ray photoelectron spectroscopy, and electron energy-loss spectroscopy measurements are presented. A clear correlation between the presence of oxygen vacancies and a saturation in cathodoluminescence response with irradiation time was also verified for both MgO(SCS) and MgO(1). These materials also demonstrate the

most pronounced mechanoluminescence signals among all materials tested. As a result, the presence of a significant amount of oxygen vacancies (correlated with the cathodoluminescence intensity saturation effect) was found to be responsible for the highest mechanoluminescent response.

4. CONCLUSIONS

A systematic analysis of the mechanoluminescence response of MgO commercial powders, together with MgO material produced by solution combustion synthesis, was performed. MgO produced by combustion synthesis was found to generate the highest mechanoluminescence response among all materials tested. Its response was about three times higher compared to the best commercially available material [*i.e.*, MgO(1)]. This pronounced difference was explained by the existence of oxygen vacancies, or F centers, as well as paired oxygen vacancies, or *M* centers. Specifically, the cathodoluminescence spectra obtained from the MgO(SCS) powders exhibited an emission at 2.04 eV associated with the presence of F^+ centers, and intense cathodoluminescence emissions at 3.70 and 4.10 eV associated with the presence of M^+ and M centers, respectively. Furthermore, cathodoluminescence measurements revealed that the mechanical stress produced on the MgO(SCS) powders by mechanoluminescence measurements, promoted the generation of a cathodoluminescence emission of 1.70 eV, which was attributed to an electronic transition between excited and ground F^+ states. Measurements of cathodoluminescence intensity with respect to irradiation time demonstrated the presence of a cathodoluminescence intensity saturation effect correlated with the presence of a high density of F^+ centers in MgO(SCS) and MgO(1) samples, which explains their highest mechanoluminescence signal. More specifically, the effect of intensity saturation with an

irradiation time during cathodoluminescence analysis was evaluated and correlated with the

presence of oxygen vacancies. The existence of the above mentioned saturation effect was found

to be one of the main features responsible for the most pronounced mechanoluminescence signal

in the MgO(SCS) powders. These findings play an important role in the understanding of

fundamental mechanisms behind the mechanoluminescence response of oxide materials, with

implications for the use of these materials in structural health monitoring applications.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/ Tables S1-2 listing powder impurities; Figures S1-3 showing scanning electron micrographs, survey X-ray photoelectron spectra, and decay time curves for the MgO powders.

AUTHOR INFORMATION

Corresponding Authors

Olivia A. Graeve — Department of Mechanical and Aerospace Engineering, University of California San Diego, La Jolla, CA 92093-0411, United States; orcid.org/0000-0003-3599-0502; Email: ograeve@ucsd.edu; URL: http://graeve.ucsd.edu/

Manuel Herrera — Centro de Nanociencias y Nanotecnología, Universidad Nacional Autónoma de México Ensenada, Baja California, México; orcid.org/0000-0002-7179-654X; Email: zaldivar@cnyn.unam.mx

Authors

 Ekaterina Novitskaya — Department of Mechanical and Aerospace Engineering, University of California San Diego, La Jolla, CA 92093-0411, United States
 Aaron Manheim — Department of Mechanical and Aerospace Engineering, University of California San Diego, La Jolla, CA 92093-0411, United States

Notes

The authors declare no competing financial interests.

ACKNOWLEDGMENTS

This work was supported by a grant from the National Science Foundation (No. 1334160) and grants from PAPIIT-UNAM (No. IN104414) and CONACYT (No. 284667). We acknowledge the use of the UC San Diego Cryo-Electron Microscopy Facility, which is supported by NIH grants and a gift from the Agouron Institute, as well as the use of the Nano3 facility, which is supported by a National Science Foundation National Nanotechnology Coordinated Infrastructure grant. The technical support of D. Domínguez is greatly appreciated.

REFERENCES

- Chandra, B. P. Squeezing light out of crystals: Triboluminescence. *Nucl. Tracks Radiat. Meas.* 1985, *10*, 225-241.
- (2) Zink, J. I. Triboluminescence. Acc. Chem. Res. 1978, 8, 290-295.
- Langford, S. C.; Dickinson, J. T.; Jensen, L. C. Simultaneous measurement of the electron and photon emission accompanying fracture of single-crystal MgO. *J. Appl. Phys.* 1987, *62*, 1437-1449.
- (4) Beese, W.; Zink, J. I. The intensity of triboluminescence. J. Lumin. 1984, 29, 119-122.
- (5) Fontenot, R. S.; Bhat, K. N.; Hollerman, W. A.; Aggarwal, M. D. Triboluminescent materials for smart sensors. *Mater. Today* 2011, 14, 292-293.
- Jha, P.; Chandra, B. P. Survey of the literature on mechanoluminescence from 1605 to 2013. *Luminescence* 2014, *29*, 977-993.
- (7) Chandra, B. P.; Rathore, A. S. Classification of mechanoluminescence. *Cryst. Res. Technol.* 1995, *30*, 885-896.
- (8) Bredikhin, S. I.; Shmurak, S. Z. Interaction of charge dislocations with luminescence centers in ZnS crystals. J. Exp. Theor. Phys. 1979, 49, 520.
- (9) Bredikhin, S. I.; Shmurak, S. Z. The luminescence and electrical characteristics of ZnS crystals undergoing plastic deformation. *Sov. Phys JETP.* **1977**, *46*, 768-773.
- (10) Zakrevskii, V. A.; Shul'diner, A. V. Electronic excitations owing to plastic deformation of ionic crystals. *Phys. Solid State* **1999**, *41*, 817-819.
- (11) Florez, E.; Fuentealba, P.; Mondragon, F. Chemical reactivity of oxygen vacancies on the MgO surface: Reactions with CO₂, NO₂ and metals. *Catal. Today* 2008, *133-135*, 216–222.

- (12) Janet, C. M.; Viswanathan, B.; Viswanath, R. P.; Varadarajan, T. K. Characterization and photoluminescence properties of MgO microtubes synthesized from hydromagnesite flowers. *J. Phys. Chem. C* 2007, *111*, 10267-10272.
- Li, M.; Wang, X.; Li, H.; Di, H.; Wu, X.; Fang, C.; Yang, B. Preparation of photoluminescent single crystalline MgO nanobelts by DC arc plasma jet CVD. *Appl. Surf. Sci.* 2013, 274, 188-194.
- (14) Novitskaya, E.; Kelly, J. P.; Bhaduri, S.; Graeve, O. A. A review of solution combustion synthesis: an analysis of parameters controlling powder characteristics. *Int. Mater. Rev.*2020, in print. DOI: 10.1080/09506608.2020.1765603
- (15) Zavala, L. A.; Fernandez, P.; Novitskaya, E.; Diaz, J. N.; Herrera, M.; Graeve, O. A. Interconfigurational and intraconfigurational transitions of Yb²⁺ and Yb³⁺ ions in hydroxyapatite: A cathodoluminescence study. *Acta Mater.* 2017, *135*, 35-43.
- (16) Zavala-Sanchez, L. A.; Hirata, G. A.; Novitskaya, E.; Karandikar, K.; Herrera, M.;
 Graeve, O.A. Distribution of Eu²⁺ and Eu³⁺ ions in hydroxyapatite: A
 cathodoluminescence and Raman study. *ACS Biomater. Sci. Eng.* 2015, *1*, 1306-1313.
- (17) Higgins, B.; Graeve, O. A.; Edwards, D. D. New methods for preparing submicrometer powders of the tungstate-ion conductor Sc₂(WO₄)₃ and its Al and In analogs. *J. Am. Ceram. Soc.* 2013, *96*, 2402-2410.
- (18) Kanakala, R.; Escudero, R.; Rojas-George, G.; Ramisetty, M.; Graeve, O. A. Mechanisms of combustion synthesis and magnetic response of high-surface-area hexaboride compounds. *ACS Appl. Mater. Interfaces* **2011**, *3*, 1093-1100.

- (19) Kanakala, R.; Rojas-George, G.; Graeve, O. A. Unique preparation of hexaboride nanocubes: A first example of boride formation by combustion synthesis. *J. Am. Ceram. Soc.* 2010, *93*, 3136-3141.
- (20) Graeve, O. A.; Kanakala, R.; Madadi, A.; Williams, B. C.; Glass, K. C. Luminescence variations in hydroxyapatites doped with Eu²⁺ and Eu³⁺ ions. *Biomaterials* 2010, *31*, 4259-4267.
- (21) Sinha, K.; Pearson, B.; Casolco, S. R.; Garay, J. E.; Graeve, O. A. Synthesis and consolidation of BaAl₂Si₂O₈:Eu. Development of an integrated process for luminescent smart ceramic materials. *J. Am. Ceram. Soc.* **2009**, *92*, 2504-2511.
- (22) Graeve, O. A.; Varma, S.; Rojas-George, G.; Brown, D. R.; Lopez, E. A. Synthesis and characterization of luminescent yttrium oxide doped with Tm and Yb. *J. Am. Ceram. Soc.* 2006, *89*, 926-931.
- (23) Shea, L. E.; McKittrick, J.; Lopez, O. A.; Sluzky, E.; Phillips, M.L.F. Advantages of self-propagating combustion reactions for synthesis of oxide phosphors. *J. Soc. Inf. Disp.* 1997, *5*, 117-125.
- (24) Shea, L. E.; McKittrick, J.; Lopez, O. A.; Sluzky, E. Synthesis of red-emitting, small particle size oxide luminescent oxides using an optimized combustion process. *J. Am. Ceram. Soc.* **1996**, *79*, 3257-3265.
- (25) Lopez, O. A.; McKittrick, J.; Shea, L. E. Fluorescence properties of polycrystalline Tm³⁺-activated Y₃Al₅O₁₂ and Tm³⁺-Li⁺ co-activated Y₃Al₅O₁₂ in the visible and near IR ranges. *J. Lumin.* **1997**, *71*, 1-11.
- (26) Hofer, F. Determination of inner-shell cross-sections for EELS-quantification. *Microsc. Microanal. Microstruct.* 1991, *2*, 215-230.

- (27) Su, D. S.; Wang, H. F.; Zeitler, E. The influence of plural scattering on EELS elemental analysis. *Ultramicroscopy* **1995**, *59*, 181-190.
- (28) Fathi, H.; Kelly, J. P.; Vasquez, V. R.; Graeve, O. A. Ionic concentration effects on reverse micelle size and stability: Implications for the synthesis of nanoparticles. *Langmuir* 2012, *28*, 9267-9274.
- (29) Cahill, J. T.; Ruppert, J. N.; Wallis, B.; Liu, Y.; Graeve, O. A. Development of mesoporosity in scandia-stabilized zirconia: Particle size, solvent, and calcination effects. *Langmuir* 2014, *30*, 5585-5591.
- (30) Vargas-Consuelos, C. I.; Seo, K.; Camacho-Lopez, M.; Graeve, O. A. Correlation between particle size and Raman vibrations in WO₃ powders. *J. Phys. Chem. C* 2014, *118*, 9531-9537.
- (31) Graeve, O. A.; Fathi, H.; Kelly, J. P.; Saterlie, M. S.; Sinha, K.; Rojas-George, G.;
 Kanakala, R.; Brown, D. R.; Lopez, E. A. Reverse micelle synthesis of oxide
 nanopowders: Mechanisms of precipitate formation and agglomeration effects. *J. Colloid Interface Sci.* 2013, 407, 302-309.
- (32) Saterlie, M.; Sahin, H.; Kavlicoglu, B.; Liu, Y.; Graeve, O. Particle size effects in the thermal conductivity enhancement of copper-based nanofluids. *Nanoscale Res. Lett.*2011, 6, 217.
- (33) Saterlie, M. S.; Sahin, H.; Kavlicoglu, B.; Liu, Y.; Graeve, O. A. Surfactant effects on dispersion characteristics of copper-based nanofluids: A dynamic light scattering study. *Chem. Mater.* 2012, *24*, 3299-3306.

- (34) Vasquez, V. R.; Williams, B. C.; Graeve, O. A. Stability and comparative analysis of AOT/water/isooctane reverse micelle system using dynamic light scattering and molecular dynamics. *J. Phys. Chem. B* 2011, *115*, 2979-2987.
- (35) Graeve, O. A.; Madadi, A.; Kanakala, R.; Sinha, K. Analysis of particle and crystallite size in tungsten nanopowder synthesis. *Metall. Mater. Trans. A* **2010**, *41*, 2691-2697.
- (36) Sinha, K.; Kavlicoglu, B.; Liu, Y.; Gordaninejad, F.; Graeve, O. A. A comparative study of thermal behavior of iron and copper nanofluids. *J. Appl. Phys.* **2009**, *106*, 064307.
- (37) Graeve, O. A.; Sinha, K. Dynamic light scattering study of reverse micellar systems for the synthesis of iron-based nanofluids. *Int. J. Mod. Phys. B* **2007**, *21*, 4774-4781.
- (38) Goedeke, S. M.; Hollerman, W. A.; Allison, S. W.; Fontenot, R. S. Detection of low-velocity-impact triboluminescent emissions. *Triboluminescence* 2016, 333-350. DOI: 10.1007/978-3-319-38842-7_11
- (39) Venkatesware Rao, K.; Sunandana, C. S. Structure and microstructure of combustion synthesized MgO nanoparticles and nanocrystalline MgO thin films synthesized by solution growth route. *J. Mater. Sci.* 2008, *43*, 146-154.
- (40) Prada, S.; Giordano, L.; Pacchioni, G. Charging of gold atoms on doped MgO and CaO:
 Identifying of key parameters by DFT calculations. *J. Phys. Chem. C* 2013, *117*, 9943-9951.
- (41) Aramburu, J. A.; García-Fernández, P.; Barriuso, M. T.; Moreno, M. Transition metal complexes coupled to vacancies in oxides: Origin of different properties of Cr³⁺ in MgO bounded to a <100> or <110> Mg²⁺ vacancy. *J. Phys. Chem. A* 2013, *117*, 12642-12647.
- (42) Herrera-Zaldivar, M.; Fernández P.; Piqueras, J. Influence of deformation on the luminescence of GaN epitaxial films. *Semicond. Sci. Technol.* **1998**, *13*, 900-905.

- (43) Nelin, C. J.; Uhl, F.; Staemmler, V.; Bagus, P. S.; Fujimori, Y.; Sterrer, M.; Kuhlenbeck
 H.; Freund, H. J. Surface core-level binding energy shifts for MgO(100). *Phys. Chem. Chem. Phys.* 2014, *16*, 21953-21956.
- (44) Kumar, M.; Kumar, A.; Thapa, S. B.; Christiansen, S.; Singh, R. XPS study of triangular GaN nano/micro-needles grown by MOCVD technique. *Mater. Sci. Eng., B* 2014, *186*, 89-93.
- (45) Al-Mamoori, A.; Lawson, S.; Rownaghi A. A.; Rezaei, F. Improving adsorptive performance of CaO for high temperature CO₂ capture through Fe and Ga doping. *Energy Fuels* 2009, *33*, 1404-1413.
- (46) Maoz, B. M.; Tirosh, E.; Bar Sadan, M.; Popov, I.; Rosenberg, Y.; Markovich, G. Highly defective MgO nanosheets from colloidal self-assembly. *J. Mater. Chem.* 2011, *21*, 9532-9537.
- (47) Maoz, B. M.; Tirosh, E.; Bar Sadan, M.; Markovich, G. Defect-induced magnetism in chemically synthesized nanoscale sheets of MgO. *Phys. Rev. B* 2011, *83*, 161201(R).
- (48) Xi, J.; Liu, B.; Zhang Y.; Weber, W. J. *Ab initio* study of point defects near stacking faults in 3C-SiC. *Comput. Mater. Sci.* 2016, *123*, 131-138.
- (49) Xi, J.; Liu, B.; Yuan, F.; Zhang Y.; Weber, W. J. Diffusion of point defects near stacking faults in 3C-SiC via first-principles calculations. *Scr. Mater.* 2017, *139*, 1-4.
- (50) Gerthsen, D.; Litvinov, D.; Gruber, Th.; Kirchner, C.; Waag, A. Origin and consequences of a high stacking fault density in epitaxial ZnO layers. *Appl. Phys. Letts.* 2002, *81*, 3972-3974.
- (51) Travlos, A.; Boukos, N.; Chandrinou, C.; Kwack H.-S.; Dang, L. S. Zinc and oxygen vacancies in ZnO nanorods. J. Appl. Phys. 2009, 106, 104307.

- (52) Schlegel, G.; Bohnenberger, J.; Potapova I.; Mews, A. Fluorescence decay time of single semiconductor nanocrystals. *Phys. Rev. Lett.* **2002**, *88*, 137401.
- (53) Hollerman, W. A.; Goedeke, S. M.; Bergeron, N. P.; Muntele, C. I.; Allison S. W.; Ila, D. Effects of proton irradiation on triboluminescent materials such as ZnS:Mn. *Nucl. Instrum. Methods Phys. Res., Sect. B* 2005, *241*, 578-582.
- (54) Choudhury, B.; Basyach, P.; Choudhury, A. Monitoring *F*, *F*⁺ and *F*²⁺ related intense defect emissions from nanocrystalline MgO. *J. Lumin.* 2014, *149*, 280-286.
- (55) Schleicher, F.; Halisdemir, U.; Lacour, D.; Gallart, M.; Boukari, S.; Schmerber, G.;
 Davesne, V.; Panissod, P.; Halley, D.; Majjad, H.; et al. Localized states in advanced dielectrics from the vantage of spin- and symmetry-polarized tunnelling across MgO. *Nat. Commun.* 2014, *5*, 4547.
- (56) MacLean, S. G.; Duley, W. W. Photoluminescence from surface states in MgO and CaO powders. J. Phys. Chem. Solids 1984, 45, 227-235.
- (57) Gonzalez, R.; Chen, Y.; Ballesteros, C.; Liu, H.; William, G. P.; Rosenblatt, G. H.;
 Williams, R. T.; Gellermann, W. Luminescence properties of deformed CaO crystals. *Phys. Rev. B* 1993, 47, 4910-4915.
- (58) Zhang, J.; Zhang, L. Intensive green light emission from MgO nanobelts. *Chem. Phys. Lett.* 2002, *363*, 293-297.
- (59) Arthur, J. S. The specific heats of MgO, TiO₂, and ZrO₂ at high temperatures. *J. Appl. Phys.* 1950, *21*, 732.
- (60) Sousa, C.; Pacchioni G.; Illas, F. Ab initio study of the optical transitions of F centers at low-coordinated sites of the MgO surface. *Surf. Sci.* **1999**, *429*, 217-228.

- (61) Rosenblatt, G. H.; Rowe, M. W.; Williams, G. P.; Williams, R. T.; Chen, Y.
 Luminescence of F and F⁺ centers in magnesium oxide. *Phys. Rev. B* 1989, *39*, 10309-10318.
- (62) Popov, A. I.; Shirmane, L.; Pankratov, V.; Lushchik, A.; Kotlov, A.; Serga, V. E.;
 Kulikova, L. D.; Chikvaidze, G.; Zimmermann, J. Comparative study of the
 luminescence properties of macro- and nanocrystalline MgO using synchrotron radiation. *Nucl. Instrum. Methods Phys. Res., Sect. B* 2013, *310*, 23-26.
- (63) Feldbach, E.; Jaaniso, R.; Kodu, M.; Denks, V. P.; Kasikov, A.; Liblik, P.; Maaroos, A.;
 Mändar, H.; Kirm, M. Luminescence characterization of ultrathin MgO films of high crystallinity prepared by pulsed laser deposition. *J. Mater. Sci. Mater. Electron.* 2009, 20, 321-325.
- (64) Rinke, P.; Schleife, A.; Kioupakis, E.; Janotti, A.; Rödl, C.; Bechstedt, F.; Scheffler, M.;
 Van de Walle, C. G. First-principles optical spectra for F centers in MgO. *Phys. Rev. Lett.*2012, *108*, 126404.
- (65) Domínguez-Ariza, D.; Sousa, C.; Illas, F.; Ricci, D.; Pacchioni, G. Ground- and excitedstate properties of M-center oxygen vacancy aggregates in the bulk and surface of MgO. *Phys. Rev. B* 2003, *68*, 054101.
- (66) Liu, Y.; Lin, Y.-M.; Yang, S.-F. A thermodynamic interpretation of the Monod equation. *Curr. Microbiol.* 2003, *46*, 233-234.
- (67) Jonnard, P.; Bonnelle, C.; Blaise, G.; Rémond, G.; Roques-Carmes, C. F⁺ and F centers in α-Al₂O₃ by electron-induced x-ray emission spectroscopy and cathodoluminescence. *J. Appl. Phys.* 2000, *88*, 6413-6417.

TOC Graphic

