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Light emission induced by electric current at room temperature through the defect networks of MgO nanocubes

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ABSTRACT
Magnesium oxide (MgO) is generally a wide band-gap oxide unable to conduct electric current in the bulk at room temperature. In this study, MgO nanocubes synthesized by self-burning micro-sized Mg metal powders in air showed electrical conductivity when they were sandwiched between two gold-mesh electrodes and steadily applied a voltage at room temperature (∼25°C). In addition, a simultaneous light emission caused by the microdischarge of nitrogen molecules occurred adjacent to the cathode. The light emission was observed when traces of water vapor existed in the gas environment. In the case of a voltage pulse produced by switching off, transient emissions of Mg I and Mg II were detected on both sides of the electrodes. However, those steady and transient light emissions were not observed in the commercial MgO nanoparticles devoid of nanocubes. The light emissions shown in the cases of the steady-state might be caused by electron injection into the empty conductive states, which exist along the edges of MgO nanocubes, as a result of the spontaneous dissociation of water vapors at reactive sites of the nanocube surfaces as well as a result of the reduction of the energy barriers between the cathode and MgO nanocubes in contact. For transient emission, electrons trapped in the low coordinate sites were released with voltage pulse and neutralized the nearby Mg+ and Mg2+ ions, driving them into the excited neutral states, Mg I and Mg II.

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I. INTRODUCTION

Metal oxide nanoparticles have been intensively investigated for applications as gas adsorbents, catalysts, medicine, electronics, gas sensors, new regeneration energy materials, etc. In particular, magnesium oxide (MgO) is an extremely studied material1–4 because of its attractive characteristics, such as ionic crystals with a cubic rock-salt structure (e.g., NaCl) consisting of Ne-like cores charged with Mg2+ and O2−. In contrast, the chemical bond in the MgO molecule is much more covalent than that in the bulk crystal, and the effective charges on the ions composing the molecule are Mg+ and O−. In the bulk MgO crystal, the electron affinity is practically eliminated by the Madelung potential. In addition, bulk MgO is not electrically conductive with a band-gap of 7.7 eV, which was measured from cathodoluminescence and synchrotron radiations.1

For crystalline MgO nanoparticles with a cubic shape (nanocubes), the electric current can flow through the contact sites (CSs) between the nanocubes consisting of low coordinates (LCs). Indeed, the Madelung potential decreases rapidly as the Mg and O coordination reduces, thus adjusting the electron affinity comparable to the electron affinity of a free ion for the Mg ion at the edge, corner, and other LC sites.5,6 The calculated relaxed electron affinities of 3-coordinated Mg sites of 1–2 eV demonstrate that they can serve as electron traps.7,8 A trapped electron is almost entirely localized at the terminating Mg ion, thus becoming...
similar to Mg⁺. Therefore, it is likely that three- and four-coordinated ions on the surface of MgO nanocubes being in some intermediate charge state may create the band-gap states⁷–⁹ that can conduct electrons, which are injected into the states. If its valence bands are completely filled and conduction bands are empty, the MgO crystal would transfer an electric current of electrons and holes only along the LC features—mostly edges. In this study, we found novel electrical conductivity through the defect networks of MgO nanocubes at room temperature (∼25°C) caused by charge injection in a sandwich structure and observed light emission followed by electric current.

II. EXPERIMENT

Figure 1 shows a scanning electron microscopy (SEM) image of the collected MgO nanocubes synthesized through self-burning of Mg metal chips in air¹ and four geometrically possible types of the CSs between MgO nanocubes, which are classified by the number of LCs (i.e., edges and corners) meeting at each CS. These surface features should also exhibit some molecular-like properties and produce band-gap states.⁷–⁹ If electrons are injected into the band-gap states, the electrical conductivity may occur through the LC features at CSs. However, it is known that charge injection can be a nontrivial task due to the high interface barriers and often needs sophisticated charge transferring layers, for example, for charge injection into organic materials.¹¹ Farhat et al. studied charge injection into a single MgO crystal under a high voltage. Even though the process of charge injection took several hours, the charges stayed localized near the electrodes.¹² MgO nanocubes synthesized through the self-burning method were known to have defects, which create band-gap states in the material.¹³

Figure 2 shows the experimental setup for measuring the electric current through the defect networks of MgO nanocubes and observing the light emission caused by the electric current. MgO nanocube powders were pressed between two gold (or silver) mesh electrodes having 500 μm × 500 μm window patterns with 200 μm line-width between 10 mm × 10 mm quartz glasses. From the measurements in ambient air at room temperature (∼25°C) on applying voltage varying from 0 to 2 kV by deploying a DC power supply (Model 247, Keithley Instruments, LLC), we measured the electric current (0–300 μA) through an ampere meter (Model 6517, Keithley Instruments, LLC) and observed steady-state violet-colored light...
emission exclusively from the cathode side through a spectrometer (Acton 300i, Princeton Instrument, Inc.).

III. RESULTS AND DISCUSSION

Figure 3 shows the spectrum of the steady-state light emission when DC voltages were applied to the electrodes of the experimental setup shown in Fig. 2. The light emission indicates that the total potential drop was uneven and mostly localized between the cathode and the MgO powder surface, meaning good conductivity through the rest of the powder up to the anode. When the voltage was applied steadily, it showed steady-state light emission, whose spectrum consisted of N$_2$ (C$^3Iu$ $\rightarrow$ B$^3IIg$, second positive) transition of excited neutral N$_2$ molecules with several vibration bands, the most prominent being the 337 nm $\Delta\nu = 0$ band usually used for lasing transition in N$_2$ based TEA lasers, as shown in Fig. 3. Three weak lines of N$_2^+$ (B$^2\Sigma_u^+$ $\rightarrow$ X$^2\Sigma_g^-$, first negative) can also be distinguished, which are known as the working transition for nitrogen ion charge-transfer lasers. When the ambient air was replaced by the N$_2$ gas [ultra high purity (UHP) grade] in an enclosed chamber, the electric current through the sample as well as the light emission immediately stopped in the introduced dry N$_2$ gas environment. The current and the light emission resumed when the relative humidity (RH) arrived at $\sim$50% RH at room temperature. We conjectured that the water moisture film on the cathode is responsible for electron injection by reducing the contact barriers between the cathode and the powder either due to a high static dielectric constant, $\varepsilon_W = 81$, or due to water molecule splitting near the contacts of the cubes with the electrode.

The current ($I_E$) and the light emission intensity ($I_L$) had strong voltage dependence; the latter had stronger power dependence on voltage at low voltage ranges, as shown in Fig. 4(a). The former, the current-voltage ($I$-V) curve, can be fit with $I_E \sim aV^b$, where $b \sim 4.6$ is close to $b \sim 5.6$ found in the so-called soft breakdown in MgO films. At around 1.35 kV, the current passed the maximum value and then declined, thus demonstrating negative resistance – a strong indication for trapped charges and memory effects existing in the pressurized MgO nanocube powders. Note that for commercial MgO nanoparticles (>99% purity, trace metal-based, <325 mesh, Aldrich, Co.), which have irregular shapes (not a perfect cube) and few defects, we did not observe the steady-state light emission. The current through the commercial MgO was also negligible at the applied voltage in the range of 0–2 kV. One can compare the situation with the very low current observed through MgO thin films that occurred due to F (oxygen vacancy) and V (Mg vacancy) centers in the bulk of MgO. This comparison supports the percolation mechanism of the electron transport via LC edges and CSs between MgO nanocubes sandwiched by the two electrodes.

The $I_L$ in all the spectral bands was closely proportional to the square of $I_E$ [Fig. 4(b) shows the correlation between $I_L$ and $I_E^2$.
$I_E$ for a representative line at 337 nm], which indicates that it is the electron-ion recombination $N_2^+(X^2\Sigma_g^+)+e\rightarrow N_2 (C^3Π_u)\Rightarrow N_2(B^3Π_u)+hν$ that is responsible for the glow from neutral $N_2$ molecules and electron-ion collision $N_2^+(X^2\Sigma_g^+)+e\rightarrow N_2^+(B^2Σ_u^+)+e+hν$ that is responsible for the emission from $N_2^+$ ions.\textsuperscript{14} As far as no glow was seen near the anode, we conclude that the injected electrons were directly transmitted from the powder to the metal of the anode being different from the cathode side.

Those LC sites that trap electrons (mostly Mg-terminated corners\textsuperscript{1}) were able to be selectively excited by the electric pulse in the MgO nanocubes, which resulted in transient luminescence spectra, as shown in Fig. 5. The voltage pulse was generated by switching off the power supply (at 2 kV) and the steady-state current. This pulse up to $\sim 2$ kV was capable of releasing the electrons trapped inside the MgO nanocubes during charge injection. The spectrum of the strong transient light emission resulting from the voltage pulse consisted of the lines of Mg $\parallel$ atoms and Mg $\parallel$ ions. The transient light emission came from both cathode and anode sides and did not involve the discharge of nitrogen neutral molecules. A negligible light emission from MgO molecules\textsuperscript{24} could be distinguished near 500 nm unlike the emission observed in a flashover spectrum from alumina\textsuperscript{−} in which the bands of AlO were the major bands.

The two observed transient bands (384 nm and 518 nm) were seen before from MgO powder under the pulsed Nd YAG laser irradiation, but poorly resolved. They were prescribed to lasing in the MgO powders.\textsuperscript{25,26} However, our high resolution spectra demonstrate fine structures of the 384 nm triplet Mg $\parallel$ (3 $^1Π_{1/2,3/2}→ 3^3P_{1/2,1/2}$) and the 518 nm triplet Mg $\parallel$ (4 $^3Σ_1−→ 3^3P_{0,1,2}$) (both lines have the same triplet ground state $3^3P_{0,1,2}$).\textsuperscript{27} We also saw strong lines at 280 nm [two doublets (3 $^3P_{1/2,3/2}→ 3^3S_{1/2}$) and (3 $^3D_{3/2,5/2}→ 3^1P_{1/2,2,3/2}$) of Mg $\parallel$ which came from two $3^3P_{1/2,3/2}$ levels] and at 285 nm [a singlet of Mg $\parallel$ (3 $^1P_{1}→ 3^1S_0$)] that were not detected in Refs. 13 and 14. Interestingly, the 518 nm line can indeed produce lasing in the Mg vapor, for example, if the transition at 285 nm is resonantly pumped with an ultraviolet laser.\textsuperscript{28} This occurs because the upper level of 518 nm triplet $4^3Σ_1$ is at 41 197.4 cm$^{-1}$, while the upper level of 285 nm line $3^1P_1$ is at 35 051.26 cm$^{-1}$ that is only 0.76 eV lower. The levels are sufficiently close to expect the electrons from the 285 nm upper level to overpopulate the 518 nm upper level and induce lasing. We expect that the lasing scheme may work in our system as well.

According to Beck et al.,\textsuperscript{30} there is a mechanism invoked to explain neutral Mg $\parallel$ atom desorption that can be used for understanding why the Mg $\parallel$ and Mg $\parallel$ lines are excited in our transient light emission experiment, but still we do not have any desorption (see also Refs. 13 and 14). Indeed, the electrons trapped in the LC sites were released with the voltage pulse and neutralized the nearby Mg$^+$ and Mg$^{2+}$ ions, driving them into the excited neutral states Mg $\parallel$ and Mg $\parallel$. However, the neutral atoms were not desorbed and stay attached to the crystal. The Fano-type spectral lines of the 518 nm band (Mg $\parallel$) were clearly seen, as seen in Fig. 5, and demonstrated the bound state of Mg $\parallel$ atoms in the MgO nanocubes at various excitation intensities. The Fano-type asymmetry in the spectral lines (518 nm, Mg $\parallel$) shown in Fig. 5 corresponds to the Fano parameter $q = 12$. This parameter coupled the Mg $\parallel$ transitions with the pseudocontinuum levels that may come from trapped electrons, which neutralize and excite the ions. All three lines were grown proportionally with the excitation pulse, which indicates the absence of any lasing phenomena at least at the present excitation levels. Therefore, it seems that the findings in Refs. 13 and 14 about the lasing in the MgO powders was only the demonstration of the threshold effect of Mg $\parallel$ excitation on the LC sites of MgO powders.

![FIG. 5. Spectra of the transient light emission for two kinds of mesh electrodes, Au (red) and Ag (blue) (switched off at 2 kV): the weak lines come from Au I and Ag I emission. The high resolution spectra (0.1 nm resolution) for Mg $\parallel$ (280 nm), Mg $\parallel$ (285 nm), Mg $\parallel$ (384 nm), and Mg $\parallel$ (518 nm) are shown on the top. The evolution of the 518 nm triplet at three excitation intensities is shown as well. The classification of the lines is given in the text.](https://example.com/fig5.png)
IV. CONCLUSION

In this paper, we found the electrical conductivity of MgO nanocubes through defect networks at room temperature, which is generally not found in single crystals and which was accompanied by light emission (steady-state ones from nitrogen molecules and transient ones from MgO nanocubes) excited by the electric current in the MgO nanoparticles. Our finding of the conduction in the network of MgO nanocubes and the accompanying steady-state and transient light emissions may have applications in nano-optics, oxide electronics, and memory systems.\textsuperscript{43,44} Sharp-edged nanoparticles of other oxides\textsuperscript{34} can be envisaged to produce similar effects of edge conductivity and likely be combined with the so-called topological insulators.\textsuperscript{35}

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