

# Pressure-induced photoluminescence of MgO

Xin Li<sup>1,2</sup>, Ye Yuan<sup>2</sup>, Jinbo Zhang<sup>2,3</sup>, Taehyun Kim<sup>4</sup>, Dongzhou Zhang<sup>5</sup>,  
Ke Yang<sup>6</sup>, Yongjae Lee<sup>2,4</sup> and Lin Wang<sup>2,7</sup> 

<sup>1</sup> Department of Physics, Fudan University, Shanghai 200433, People's Republic of China

<sup>2</sup> Center for High Pressure Science and Technology Advanced Research, Shanghai, 201203, People's Republic of China

<sup>3</sup> College of Physical Science and Technology, Yangzhou University, Yangzhou 225002, People's Republic of China

<sup>4</sup> Department of Earth System Sciences, Yonsei University, Seoul, Republic of Korea

<sup>5</sup> Hawai'i Institute of Geophysics and Planetology, School of Ocean and Earth Science and Technology, University of Hawai'i at Manoa, Honolulu, 96822, United States of America

<sup>6</sup> Shanghai Institute of Applied Physics, Chinese Academy of Sciences, Shanghai 201203, People's Republic of China

E-mail: [wanglin@hpstar.ac.cn](mailto:wanglin@hpstar.ac.cn)

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## Abstract

It is reported in this paper that pressure can promote strong photoluminescence (PL) in MgO. The PL measurements of MgO indicate that it has no obvious luminescence at pressures lower than 13 GPa. PL starts to appear upon further compression and reaches a maximum intensity at about 35 GPa. The center of the emission band shows a red shift at lower pressures and turns to a blue shift as pressure exceeds 25 GPa. The PL is preserved upon complete decompression. The defects and micro-strain due to the plastic deformation of MgO are likely responsible for the origin of the luminescence.

Keywords: MgO, high pressure, photoluminescence

(Some figures may appear in colour only in the online journal)

## Introduction

Magnesium oxide (MgO), an alkaline-earth oxide with NaCl-type structure, is an important material in many areas and has received a lot of research attention. Due to its high melting point and refractory nature, MgO can serve as a refractory material and diffusion barrier in ferroelectrics materials [1]. In geoscience, ferropericlase ((Mg, Fe)O) is proposed to be the second most abundant material in the Earth's low mantle, constituting about 20% of the lower mantle volume of the Earth. Thus, it is important to the development of lower mantle and the origin of the seismic anisotropy [2, 3]. MgO is also usually used as a pressure calibrant and thermally insulating material in high-pressure and high-temperature experiments because of its thermodynamic stability and low chemical reactivity [4]. Diamond anvil cell (DAC) measurements demonstrated

that the NaCl-type structure of MgO could be stable to at least 227 GPa [5] and the calculations of its structural and elastic properties are in good agreement with the high-pressure experiments [6].

The optical properties of MgO have also attracted plenty of research interest over the past few decades. As a typical ionic compound, it has a wide band gap of 7.8 eV with high optical transmissibility. Like most metal oxides, introduction of defects or color centers could generate an extra level within the band gap and stimulate strong luminescence in MgO. Irradiation of the crystals by energetic particles was thought to be an efficient way to introduce color centers in MgO. Chen *et al* observed a luminescence band located at 3.13 eV that can be excited by UV light and x rays in irradiated MgO crystals and they attributed this luminescence to F<sup>+</sup> center (oxygen vacancy occupied by one electron) [7]. Rosenblatt *et al* suggested that another color centers in MgO, the so-called F center (oxygen ion vacancies each occupied by two electrons),

<sup>7</sup> Author to whom any correspondence should be addressed.

should be addressed together with  $F^+$  centers since they have very similar absorption bands with peaks at 247 nm for  $F$  centers and 251 nm for  $F^+$  centers [8]. Jeffries *et al* studied the luminescence in thermochemically reduced MgO and long-life luminescence or phosphorescence following the excitation of  $F$  center was observed near room temperature [9]. Furthermore, two thermally-stimulated luminescence (TSL) glow peaks were found at around 90 and 140 °C in irradiated MgO from the TSL experiments [10]. However, neither irradiation nor the thermochemical reduction can only produce limited color centers in the crystals.

Pressure can generate defects, which has been proved to be a useful means to promote or improve the luminescence of wide band gap materials [11, 12]. However, the photoluminescence (PL) of MgO has not been well studied at high pressure. In this paper, we report a pressure-induced PL that has not been observed before. This luminescence band shows a maximum intensity at about 35 GPa both in the powder and single crystal MgO samples. The origin of this luminescence is also discussed.

## Experimental details

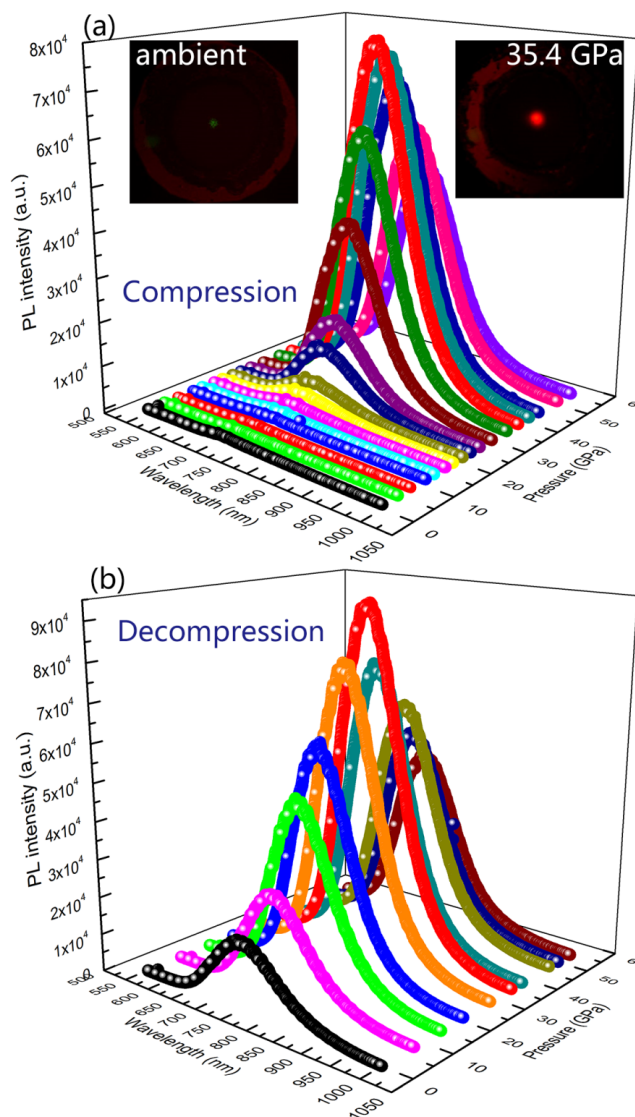
We used MgO powder with a purity of 99.99% and a MgO single crystal with a (100) orientation, respectively, as samples. X-ray fluorescence measurement was performed to analyze the possible low concentration impurities in the sample. A symmetric DAC with a culet of 300  $\mu\text{m}$  was used to perform high-pressure experiments. Gasket holes with a 120  $\mu\text{m}$  diameter were drilled in preindented steel gaskets. Silicon oil or neon was used as pressure media in the experiments. Ruby was used as the pressure calibrant and pressure was determined by its fluorescence shift with pressure.

PL spectra were recorded using a Raman spectrometer (Renishaw inVia, UK) with its fluorescence mode. A Nd: YAG laser with a wavelength of 532 nm was used to excite the luminescence in MgO under high pressure.

*In situ* high-pressure XRD experiments were employed to study the evolution of strains in MgO under high pressure. The XRD measurements were carried out at beamline 13-BM-C ( $\lambda = 0.434 \text{ \AA}$ ) of the Advanced Photon Source (APS) in the Argonne National Laboratory and beamline BL15U1 ( $\lambda = 0.6199 \text{ \AA}$ ) of the Shanghai Synchrotron Radiation Facility (SSRF) for the single crystal and powder samples, respectively. 2D AD-XRD patterns were collected using a MarCCD detector and converted to 1D XRD spectra using the Fit2D software package [13]. The full widths at half maximum (FWHMs) of the diffraction peaks were fitted using the Gaussian and Lorentz functions.

## Results and discussions

The PL of MgO powder was studied using laser excitation with a wavelength of 532 nm under high pressure. Figures 1(a) and (b) show the PL spectra of the MgO powder under the compression and decompression cycles, respectively. Upon compression, there was no obvious luminescence below 13 GPa. When the pressure reached above 13 GPa, a broad

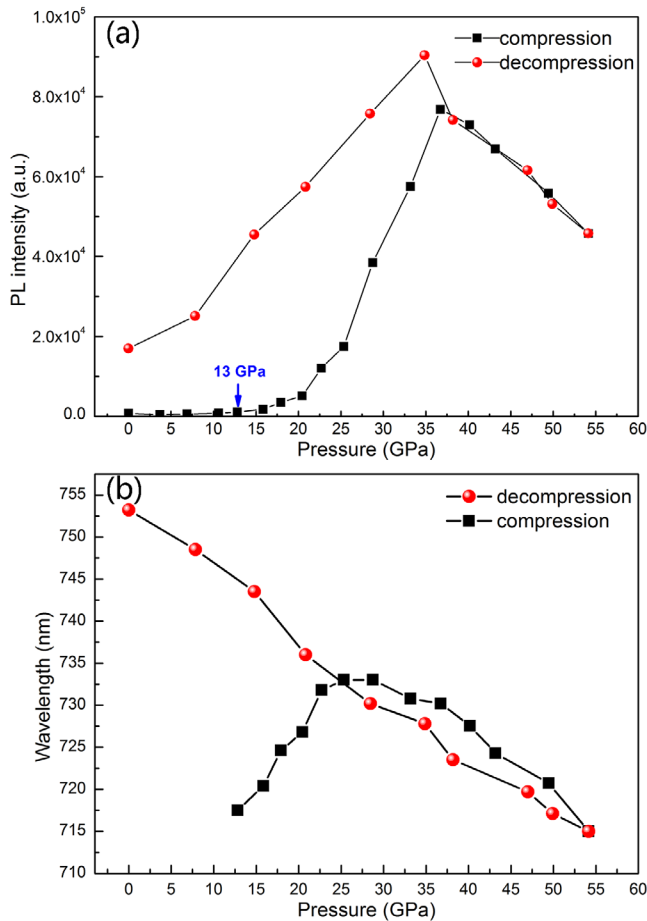


**Figure 1.** PL of powder MgO excited by a 532 nm laser under compression and decompression cycles. (a) compression, (b) decompression. The inner micro photographs shown in figure (a) taken at ambient and 35.4 GPa indicate the luminescence at high pressure.

band PL with a maximum at about 730 nm appeared and was enhanced as pressure increased. This PL reached a maximum intensity at about 35 GPa then started to decrease up to the maximum pressure of 55 GPa in our experiment.

The insert micro photographs in figure 1(a) show a direct comparison of the sample at ambient pressure and 35.4 GPa with illumination of the 532 nm laser. It is clear that the sample at ambient pressure shows no luminescence. However, the sample shows strong luminescence at 35.4 GPa, consistent with the strong signal of PL spectra. The comparison confirms the pressure-induced luminescence in MgO. Upon decompression, the PL increased first and then decreased slowly with decreasing pressure. Remarkably, the PL was preserved when the sample was quenched to ambient pressure, suggesting a potential application of MgO treated with high compression.

The pressure dependence of the intensity and peak of PL in powder MgO are presented in figure 2. The evolution of the PL

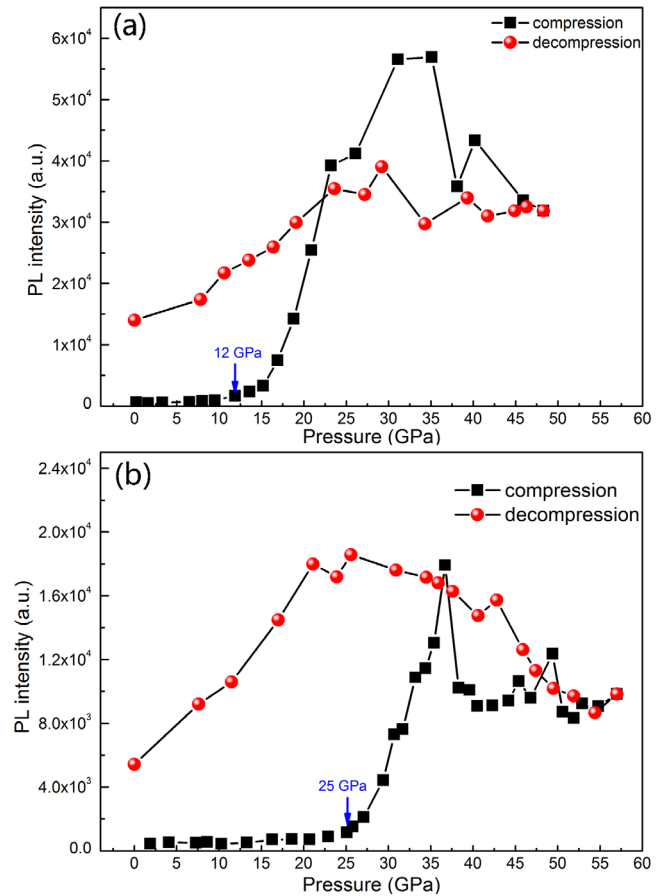


**Figure 2.** The PL intensity and peak of the MgO powder under different pressures are shown in (a) and (b), respectively. The luminescence appeared at about 13 GPa, as shown in (a).

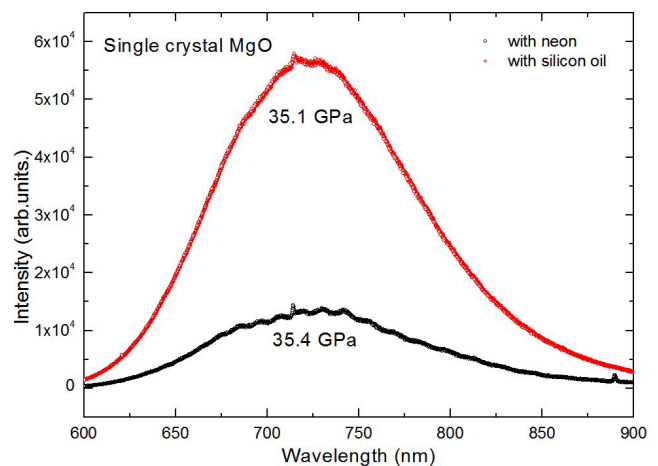
intensity under high pressure described above could be seen clearly from figure 2(a). For better understanding of this PL, we also investigate the peak of the broad luminescence under high pressure. As shown in figure 2(b), the peak of this luminescence has a red shift first with increasing pressure then turns to the blue shift at about 25 GPa. However, upon decompression, the peak shows a monotonic red shift until the pressure was completely released.

As we known, ion luminescence always has sharp emission peaks due to its distinct levels and strict selection rules. Additionally, the ion luminescence is usually suppressed or even annihilated by high pressure [14]. However, we found a very broad emission band in MgO with a FWHM of approximately 0.3 eV under high pressure above 13 GPa. Most importantly, the luminescence was significantly enhanced by pressure and recoverable during completed decompression. This suggests that the underlying mechanism of the appearance of luminescence of MgO is due to some irreversible occurrence introduced by high pressure. However, the NaCl-type structure of MgO is stable in the pressure range from ambient up to at least 227 GPa. Therefore, we suggest that the irreversible changes to the micro structure (such as defects, micro-strain, grain boundaries, etc) generated by pressure could be responsible for the observed strong luminescence.

To confirm the luminescence is not from impurities, we further studied the PL of single crystal MgO at different

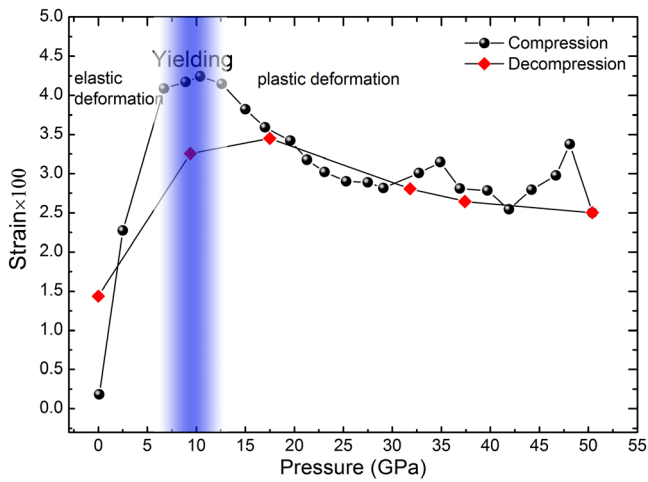


**Figure 3.** The PL intensity of the single crystal MgO under different hydrostatic pressure conditions. (a) silicon oil as pressure medium; (b) neon as pressure medium.



**Figure 4.** PL contrast of the MgO single crystal with different pressure mediums, excited by a 532 nm laser.

hydrostaticity and similar luminescence appeared in the single crystal under high pressure. Figure 3 shows the PL intensity of MgO single crystal under different hydrostatic pressure conditions. Figures 3(a) and (b) represent the PL intensity obtained in the MgO single crystal with neon and silicon oil as pressure medium, respectively. Similarly, this red luminescence appeared at high pressure and reached the maximum at about 35 GPa. Moreover, it can be seen that this red luminescence



**Figure 5.** Strains in the MgO powder under different pressures. The black solid dots and red rhombus indicate the compression and decompression processes, respectively. The crystals yielded at around 10 GPa and the plastic deformation started beyond this pressure.

appears at about 12 GPa in the sample with silicon oil and 25 GPa with neon, respectively. We also compared the PL spectra shown in figure 4 at almost the same pressure, where it reached the maximum intensity. It can be seen that stronger luminescence was obtained in the sample with silicon as a pressure medium. We suggest this big difference is due to the different pressure environments arising from the different levels of hydrostaticity. In contrast with the silicon oil, neon provides much better hydrostatic pressure conditions where the MgO single crystal undergoes elastic deformation-yielding-plastic deformation at higher pressure.

To find the correlation between the pressure-induced luminescence and compressional behavior of MgO, we carried out XRD and analyzed the development of the micro structures in MgO under high pressure [15]. As we know that strains generated by high pressures usually lead to the broadening of the diffraction peaks and the distribution of deviatoric stress along the diffraction vector. Therefore, the development of strain in the sample under high pressure can be concluded from the peaks broadening peaks [15]. The method to determine the strength from the line widths is described elsewhere and the modified equation employed in this work is given by [16]:

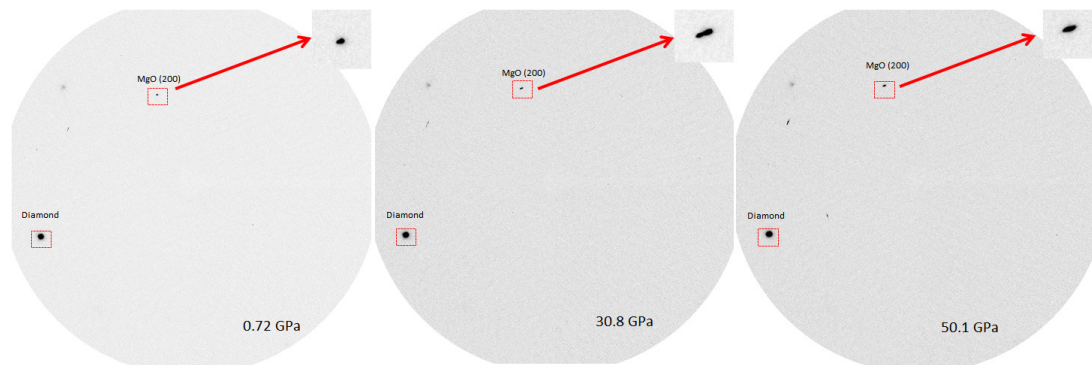
$$(2\omega_{hkl}\cos\theta_{hkl})^2 = (\lambda/d)^2 + \eta_{hkl}^2\sin^2\theta_{hkl}.$$

Where  $2\omega_{hkl}$  is FWHM of the diffraction profile on the  $2\theta$ -scale. The symbols  $d$ ,  $\lambda$ , and  $\eta_{hkl}$ , denote the grain size, x-ray wavelength, and micro-strain, respectively. The strains at different pressures are shown in figure 5. The strains increase significantly in the region from ambient to 10 GPa due to elastic deformation. During this process, grain boundaries and the density of defects (point defects, dislocations) increase as the pressure increasing. When the pressure goes up to around 10 GPa, the strain reaches the maximum and the crystals start to yield, indicating that the dislocation density in the sample reaches certain saturation and predicts an elastic-plastic deformation transition. With further compression, the point defects may annihilate and dislocations would move towards the grain boundaries and interact with others to create new

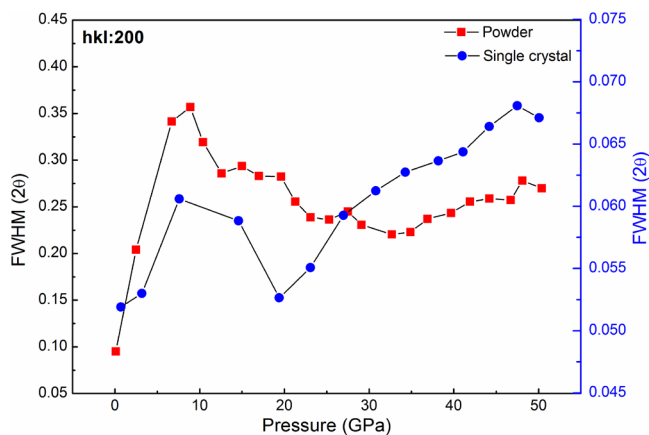
dislocations. All of these processes will lead to the decrease of the strain, and in our experiment the strain reaches a relatively stable state at about 30 GPa until the maximum pressure in our experiment. It indicates that the appearance of PL in MgO shows a close relationship to the plastic deformation process of the crystals.

Since the similar luminescence was found in the single crystal sample, we also carried out XRD experiment of single crystal. As shown in figure 6, only (200) and (220) can be obtained in our single crystal experiment due to the limit opening of DAC and the orientation of the crystal. The circular reflections of (200) and (220) at low pressures indicates the crystal keeps a good performance with less strain and defects. As the pressure increasing, the diffraction spots become broad and stretched, suggesting the evolution of strain and defects in the sample. These defects would serve as the color center and give out the luminescence. We also compared the FWHMs of diffraction peak (200) of powder and single crystal samples under compression, as shown in figure 7. It can be seen that the FWHMs undergo the similar change under high pressure in both powder and single crystalline samples. The FWHMs of single crystal also have a transition at about 10 GPa that indicates the plastic deformation starts as suggested in powder MgO. The compressional behavior of MgO we found is consistent with the observation of Merkel *et al* [17]. They suggested that the process at lower pressures is due to stress hardening for an increase in dislocation density. Beyond about 10 GPa, the hardening either stopped or slowed down. For the MgO powder, the density of dislocations will reach the maximum at about 10 GPa and after that these dislocations will move and interact with each other [18] resulting in a decrease in the strain. When this process finishes at around 30 GPa, the strain will become stable and the defects are more concentrated and can trap more electrons. In fact, pressure can not only produce defects, but also change the crystal field through lattice distortion and phase transition, which could influence the band structure, and lead to some novel optical properties, such as pressure-induced PL in  $Mn^{2+}$ -doped  $BaF_2$  and  $SrF_2$  fluorites and  $MnF_2$  [19, 20]. Therefore, combined with the PL experiment, we suggest that the crystal field and the defects process involved during plastic deformation is attribute to the PL.

From the high-pressure PL measurements of the MgO powder and single crystal, the defects and micro-strain involved in the plastic deformation period are suggested to promote the luminescence at high pressure. These defects complexes and micro-strain at high pressures could form a localized level serving as the acceptor among the band gap and lead to the radiative transition of electrons between the acceptor state and conductor band, like the luminescence of F and  $F^+$  centers, which the point defects serve as the color centers at ambient conditions [8]. On the other hand, high pressures could enhance this luminescence through changing the crystal field, which could influence the band structure and offer more opportunities for the transition. It should be noted that the defects generated by pressure should contain point defects, dislocations, grown-in dislocations and so on. Especially because, unlike at ambient pressure [21], the grown-in dislocations under high pressure may have a more influence on the luminescence in MgO. This dislocation related PL can be observed in other systems, like the several sharp luminescence peaks related to



**Figure 6.** Single crystal XRD patterns under high pressure at the same angle. The upper right corner pictures show the zoom-in (200) peak of MgO.



**Figure 7.** The FWHMs of diffraction peak (200) in powder and single crystal MgO under compression.

different dislocations in silicon [12] and luminescence from stacking faults in GaN [22].

## Conclusions

In summary, we report pressure-induced PL in MgO. The luminescence appears at about 13 GPa in the powder sample and has a maximum intensity at about 35 GPa. During compression, the center of the luminescence shows a red shift and becomes blue shift at higher pressures. The PL is preserved when the pressure was released down to ambient pressure. Defects and micro-strain introduced by plastic deformation of MgO at high pressure are suggested to be responsible for the origin of the luminescence.

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## ORCID iDs

Lin Wang  <https://orcid.org/0000-0003-2931-7629>

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