Mechanism of stimulated optical emission from MgO microcrystals with color centers

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Recently, we reported that the MgO microcrystals that are prepared via the reaction between magnesium and silicon monoxide under Ar atmosphere exhibit broadband laser emission at room temperature without using cavity mirrors under pulsed laser excitation [T. Uchino and D. Okutsu, Phys. Rev. Lett. **101**, 117401 (2008)]. Here we demonstrate that optical gain is obtained through continuous and pulsed pump and probe measurements. It has also been shown that the observed laser emission results from multiple scattering with gain in the MgO microcrystals with color centers such as F and F^+ centers. The observed stimulated optical emission has been interpreted in terms of the photoionization and the subsequent recombination processes of the color centers, which can also induce highly excited neutral states of Mg and the related atomic emissions. We suggest that the emissions from both the color centers (principally the F^+ center) and the excited neutral Mg are optically amplified by the process of multiple scattering, yielding a broad laser emission in the near-ultraviolet to blue-green spectral range.

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I. INTRODUCTION

Oxygen vacancies in metal oxides have been extensively investigated during the past decades since they can strongly improve or deteriorate some beneficial properties such as electric, electronic, and optical properties of the oxides of interest.[1,2] Among other metal oxides, MgO and its relevant oxygen vacancies have been widely studied both experimentally and theoretically because of its simple rocksalt structure.[3–7] In MgO crystals, it has been demonstrated that there exist two principal oxygen vacancies, namely, the F^+ and F color centers, which are oxygen vacancies with one and two electrons, respectively. Both the F^+ and F color centers absorb essentially the same energy of ~5 eV (~250 nm) but show different photoluminescence (PL) bands peaked at ~400 and ~500 nm, respectively.[6] The PL bands of these color centers are quite broad because the electronic states of the oxygen vacancies in such ionic crystals are tightly coupled to the crystal phonons.[8] It has hence been suggested that, although challenging, the colored MgO crystal is a potential candidate for tunable solid-state lasers operating over a considerable part of the visible spectrum.[8,9]

In our recent paper,[10] we reported the first observation of laserlike emission from the MgO microcrystals that are synthesized through the solid phase reaction between silicon monoxide (SiO) and Mg under Ar atmosphere. The thus obtained microcrystals consist mostly of the accumulated MgO crystalline cubes on the order of a few micrometers and exhibit two rather strong PL signals peaking at ~400 and ~500 nm, which are attributed to the emissions from the F^+ and F centers, as mentioned above. Stimulated emission with a threshold pump fluence of ~160 mJ/cm^2 was observed at room temperature in the near-ultraviolet to the blue-green spectral region without using cavity mirrors; however, the physical origin of the optical amplification was not fully understood. In this work, we show that the observed stimulated emission results from multiple-light scattering with gain in the luminescent MgO microcrystals. We also confirmed the optical amplification in the MgO microcrystals by pump-probe gain measurements using a continuous-wave (CW) semiconductor laser diode as a probe beam. Furthermore, it is suggested that the radiative transitions in excited neutral Mg, which is created via the photoionization of the color centers, along with the emissions from the color centers themselves are involved in the optical amplification process.

II. EXPERIMENTAL PROCEDURE

The colored MgO microcrystals were prepared using pure Mg (99.9%, ~180 μm) and SiO (99.99%, ~75 μm) powders as starting materials.[10] The SiO/Mg mixture of molar ratio 1/2 was thoroughly mixed and put in the alumina crucible. The crucible was closed with a 4 mm thick alumina lid and placed in an electric furnace. The furnace was then evacuated to a pressure down to ~30 Pa, followed by purging with argon (99.99%). The temperature of the furnace was raised to 450 °C at a rate of 7 °C/min and kept constant at 450 °C for 5 h under flowing argon environment. After the heating process, light gray powders were deposited onto the lid and the side wall of the crucible and the blue-black substances were found in the bottom of the crucible. The deposited light gray powders were found to be composed mostly of MgO with F^+ and F centers.[10] These deposited powders were carefully collected and stored in a desiccator for further use. On the other hand, the blue-black substances remained in the bottom of the crucible comprised aggregations of grains, including Mg_2Si, Si, and MgO.[10] We should note, however, that emissions related to the F^+ and F centers were hardly observed from these aggregated crystal grains although they include a substantial amount of MgO. This suggests that the MgO crystals having color centers are preferentially evaporated and deposited during the reaction between Mg and SiO.

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To evaluate whether the laserlike emission from the colored MgO powders can occur by interparticle light scattering or intraparticle resonances formed by total internal reflection at the surface of a particle, we measured the fluence-dependent emission for two different powdered samples. One of the powders consists only of the colored MgO microcrystals. The other is a mixture of α-quartz (SiO_2) (purity 99.9%; an average particle size $\sim 2-3$ μm) and the colored MgO powders, wherein the molar ratio of MgO to SiO_2 is 1:50. We confirmed that the α-quartz powder employed in this work virtually shows no PL emission under the present experimental setup. Steady state PL spectra under low-fluence excitation were recorded on a spectrofluorometer (JASCO, FP 6600) using a monochromated xenon lamp (150 W) for excitation. For high-fluence ($> \sim 20$ mJ/cm^2) excitation, samples were irradiated with the fourth harmonic (266 nm) of a Nd:yttrium aluminum garnet (Nd:YAG) laser (Spectra Physics, INDI 40) with a pulse width of 8 ns and a repetition rate of 10 Hz. The pump beam was loosely focused with an $f=150$ mm lens in such a way that the beam diameter was reduced from ~ 10 to ~ 3 mm. The focused beam was irradiated onto the powders placed in a sample holder with a 1 mm thick silica glass window. Unless otherwise noted, the measurements were carried out under ambient air atmosphere at room temperature. As for the MgO-only powder, we also carried out the PL measurement in a vacuum cell, which was evacuated down to $\sim 10^{-3}$ Pa, to evaluate a possible effect of surrounding gas molecules on the resulting PL characteristics. The pumping density of an incoming focused laser beam was continuously varied from 10 to 240 mJ/cm^2 with a variable laser beam attenuator (Metrolux, ML2100). The PL signals emitted from the sample were recorded with a spectrometer (Acton Research, Spectra Pro 300i) and a gated image-intensified charge coupled device (Princeton Instruments, PI-MAX:1024RB).

Furthermore, the enhancement of stimulated emission of MgO-only powders was studied by a pump-probe experiment. In the pump-probe measurements, a cw semiconductor laser diode (405 nm, 3.5 mW) was used as a probe beam. The pump (the fourth harmonic of a pulsed Nd:YAG laser) and probe beams were focused on the same position of the MgO-only powders. We then recorded the time-resolved emission signals from the sample with a gate delay of 0 s and a gate width of 20 ns to monitor a possible amplification of a probe beam under the following three pumping conditions:

(1) Both the pump and the probe beams on the sample, which is called $I(\lambda)_{on}$.

(2) Sample photoexcited (pump beam on the sample) but no probe beam on the sample, which is called $I(\lambda)_{off}$.

(3) No pump beam but the probe beam on the sample, which is called $I(\lambda)_{pr}$, and allows one to measure the intensity of the probe beam when the sample is not photoexcited.

Thus, the gain at a wavelength of λ of a probe beam caused by the photoexcitation of a pump beam can be estimated as $G(\lambda)=\{I(\lambda)_{on}-I(\lambda)_{off}\}/I(\lambda)_{pr}$.

III. RESULTS

A. Comparison of PL characteristics between MgO-only and MgO/SiO_2 mixture samples

When a xenon lamp is used as an excitation source, both the MgO-only and the MgO/SiO_2 mixture samples show similar broad emission bands peaking at ~ 400 and ~ 500 nm, which are attributed to the emissions from F^+ and F centers, respectively (see Fig. 1). This confirms that for low-fluence excitation the addition of SiO_2 into the colored MgO powder hardly influences the emission characteristics of the MgO microcrystals.

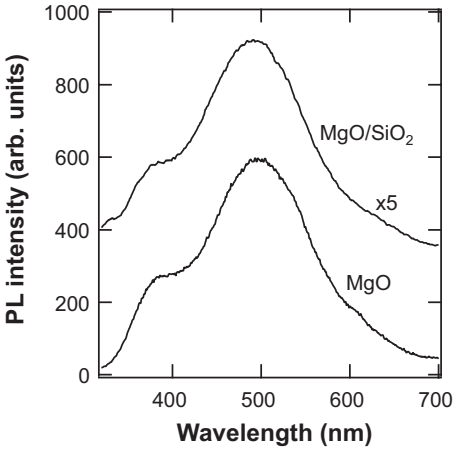

FIG. 1. PL spectra of the MgO-only (lower) powder and the MgO/SiO_2 mixture (upper) powder by excitation with a monochromated Xe lamp ($\lambda_{ex}=256$ nm). The upper spectrum is vertically shifted for clarity.

For high-fluence ($> \sim 20$ mJ/cm^2) excitation, however, the MgO-only and the MgO/SiO_2 mixture samples show different emission behaviors. Figure 2 shows the wavelength-integrated PL intensities of the two samples recorded at different pump fluences. The MgO-only powder exhibits a nonlinear increase in the PL intensity with energy fluence with a threshold fluence of ~ 160 mJ/cm^2, illustrating that, as has already been reported in Ref. 10, laserlike emission occurs in the present MgO powder. We also notice from Fig. 3(a) that in the MgO-only powder the emission intensity of the F^+ center band at ~ 400 nm preferentially increases with

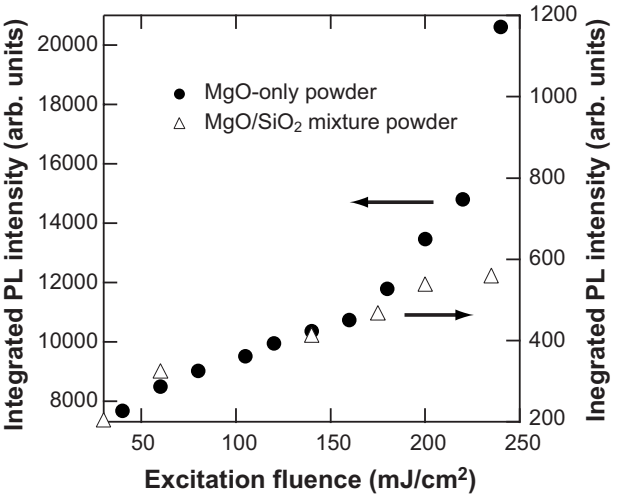

FIG. 2. The wavelength-integrated PL emission intensity of the MgO-only powder and the MgO/SiO_2 mixture powder as a function of excitation fluence. The fourth harmonic of a pulsed Nd:YAG laser ($\lambda_{ex}=266$ nm) was used as an excitation source.

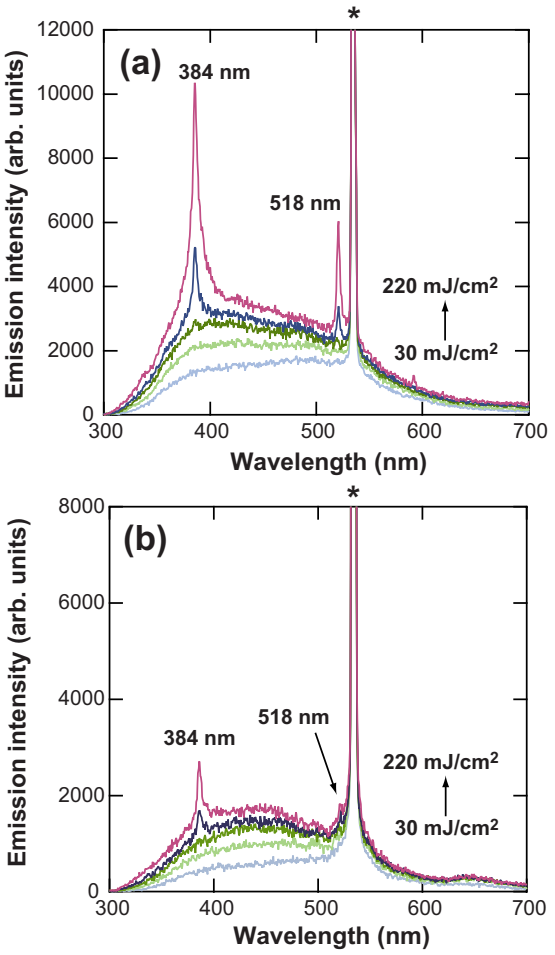

FIG. 3. (Color online) Emission spectra of (a) the MgO-only powder and (b) the MgO/SiO_2 (1/50 in molar ratio) mixture powder excited by different fluence energies. The pumping fluences are (from bottom to top) 30, 60, 140, 180, and 220 mJ/cm^2. Asterisk indicates the second harmonic (532 nm) of the Nd:YAG laser contaminated in the incident laser beam.

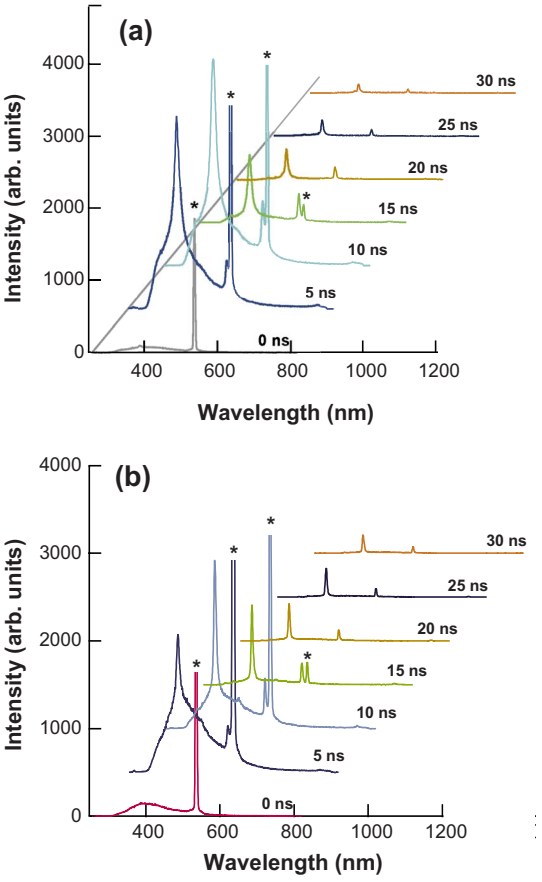

FIG. 4. (Color online) Time-resolved PL spectra of the MgO-only powder recorded (a) in air and (b) in vacuum ($<10^{-3}$ Pa) under the pumping fluence of 200 mJ/cm^2. All the spectra were recorded with a constant gate width of 5 ns using the respective gate delay times indicated. Asterisk indicates the second harmonic (532 nm) of the Nd:YAG laser contaminated in the incident laser beam. The upper spectra are vertically and horizontally shifted for clarity.

pumping fluence up to ~ 140 mJ/cm^2, probably demonstrating the amplified spontaneous emission.[10] Then, the emission signal shows a rapid increase in intensity above the threshold of ~ 160 mJ/cm^2, accompanied by the appearance of two sharp peaks at 384 and 518 nm.

On the other hand, the MgO/SiO_2 mixture shows an almost linear increase in the integrated PL intensity with pump fluence (see Fig. 2). Thus, the mixture of MgO and SiO_2 does not show a threshold behavior concerning the wavelength-integrated PL intensity, exhibiting no light amplification. We, however, notice from Fig. 3(b) that the PL spectra of the mixture powder obtained under high-fluence excitation ($>\sim 180$ mJ/cm^2) have two sharp peaks at 384 and 518 nm although a preferential increase in the emission intensity at ~ 400 nm as seen in the MgO-only sample was not observed. It is interesting to note that the wavelengths of these two peaks coincide with those of the two strong peaks observed in the amplified emission spectra of the MgO-only powder [see Fig. 3(a).] This implies that the onset of these two sharp peaks at 384 and 518 nm does not necessarily result from light amplification or lasing in the colored MgO microcrystals, as will be discussed in Sec. IV B.

B. PL characteristics of the Mg-O only sample observed in air and in vacuum

As for the Mg-O sample, the fluence dependence of the emission spectra was also obtained under vacuum ($<\sim 10^{-3}$ Pa). A laserlike behavior, namely, the preferential increase of the F^+-center band, the threshold behavior of the integrated PL intensity, and the highly nonlinear increase in the intensity of the two sharp peaks at 384 and 518 nm were observed even under vacuum conditions as well. Time-resolved measurements above the threshold clearly revealed the difference and similarity between the spectra measured under air and vacuum (see Figs. 4 and 5). It is clear from Figs. 4 and 5 that the emission spectra and their decay kinetics measured under vacuum are basically comparable to those recorded in air, indicating that the underlying excitation and emission processes of the present MgO microcrystals are hardly affected by surrounding gas molecules. Note also that a broad emission band at ~ 400 nm is evident es-

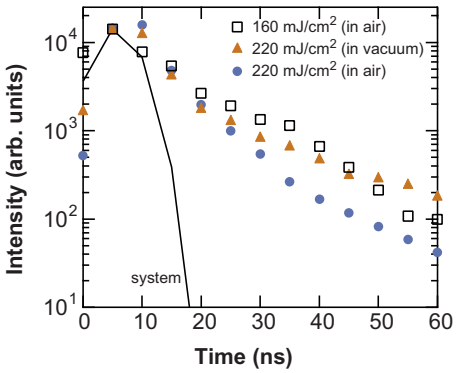

FIG. 5. (Color online) Time decay of the luminescence of the MgO-only powders at the peak wavelength of 384 nm measured under different pumping and atmospheric (vacuum and air) conditions.

pecially during irradiation of nanosecond (ns) laser pulse, probably showing an amplified and short-lived emission of the F^+ center (see also Sec. III D). Furthermore, the two sharp peaks at 384 and 518 nm develop rapidly upon nanosecond laser-pulse irradiation and then show a rapid decay within several tens of nanoseconds. It is interesting to note, however, that the half width of the peak at 384 nm measured under air atmosphere is ~10–~20 nm, whereas the corresponding half width measured under vacuum is ~6 nm. Thus, as far as the two peaks at 384 and 518 nm are concerned, a possible effect of gas collisions cannot be neglected in the relevant emission process, which will be discussed in Sec. IV B.

C. Gain measurement in a pump-probe experiment

Figure 6(a) shows the results of the gain measurements for the MgO-only sample under excitation fluence of 210 mJ/cm^2, which is above the threshold fluence of ~160 mJ/cm^2. To highlight a gain of the probe beam, the difference between $I(\lambda)_{on}$ and $I(\lambda)_{off}$ along with $I(\lambda)_{pr}$ is shown in Fig. 6(b). We see from Fig. 6(b) that the intensity of the probe beam is amplified during irradiation of the pulsed Nd:YAG laser used as a pump beam, yielding the gain $G(\lambda)$ of ~1.8 at 405 nm. This pump-probe measurement hence demonstrates that the optical amplification indeed occurs even in the wavelength region outside the sharp peaks at 384 and 518 nm, corroborating a broad band nature of the present lasing process.

Figure 6(b) further reveals a general spectral feature often found in pump-probe measurements. On the higher wavelength side of the probe beam at 405 nm, we observe a dip at ~380 nm in the $I(\lambda)_{on}-I(\lambda)_{off}$ spectrum [see the downward arrow in Fig. 6(b)] but not in the $I(\lambda)_{pr}$ spectrum. We confirmed that this dip does not result from the intensity fluctuation of the emission spectra during the measurements but always occurs concomitantly with the gain of the probe beam, implying that "gain" and "dip" are correlated with each other. Previously, similar gain and dip characteristics are observed in a pump-probe measurement of other gain materials and the features were interpreted in terms of "in-

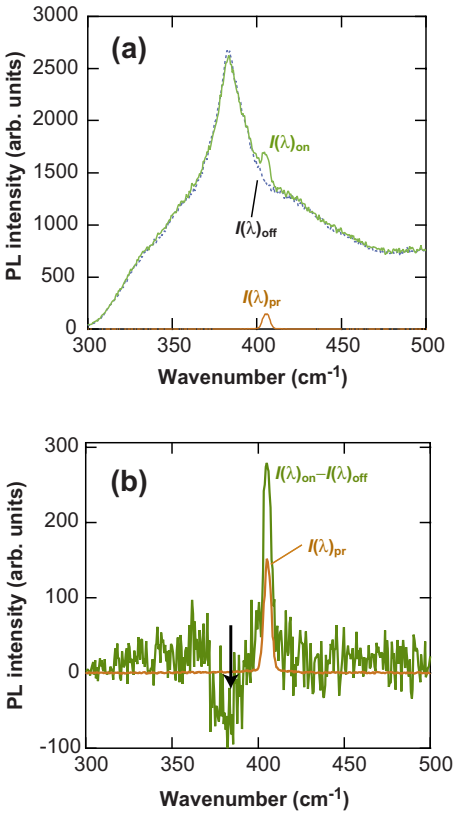

FIG. 6. (Color online) (a) Time-resolved emission spectra of the MgO-only powders under pump excitation, $I(\lambda)_{off}$, under pump and probe excitations, $I(\lambda)_{on}$, and under probe irradiation, $I(\lambda)_{pr}$. Emission signals were taken with a gate delay of 0 s and a gate width of 20 ns under the pump fluence of 210 mJ/cm^2. (b) The difference spectrum between $I(\lambda)_{on}$ and $I(\lambda)_{off}$. The signal only from the probe beam, $I(\lambda)_{pr}$, is also shown.

tensity transfer" from the energy level of dip to that of gain.[11] Thus, the observation of dip in the $I(\lambda)_{on}$ spectrum is not inconsistent with the observation of gain.

D. Comparison between the decay dynamics below and above the threshold fluence

To confirm a possible change in the decay time with excitation fluence we measured the time-resolved PL spectra of the MgO-only powders below and above the amplification threshold (see Fig. 7). When the incident pump fluence is well below the threshold, the PL spectrum obtained with a gate width of 20 ms is almost unchanged irrespective of gate delay time t_d as long as t_d is below several tens of nanoseconds [see Fig. 7(a)]. This result indicates that the decay time of the emission bands attributed to the F^+ (~400 nm) and F (~500 nm) centers is longer than at least ~100 ns, in agreement with the long-lived nature of the spontaneous emissions from the F-type centers. In contrast, as shown in Fig. 7(b), the excitation above the threshold fluence results in a substantial change in the emission spectrum with t_d; that is, the broad emission feature and the sharp emissions at 384 and 518 nm exhibit a sudden decrease in intensity by changing a gate delay time from 0 to 35 ns. Such a short-lived

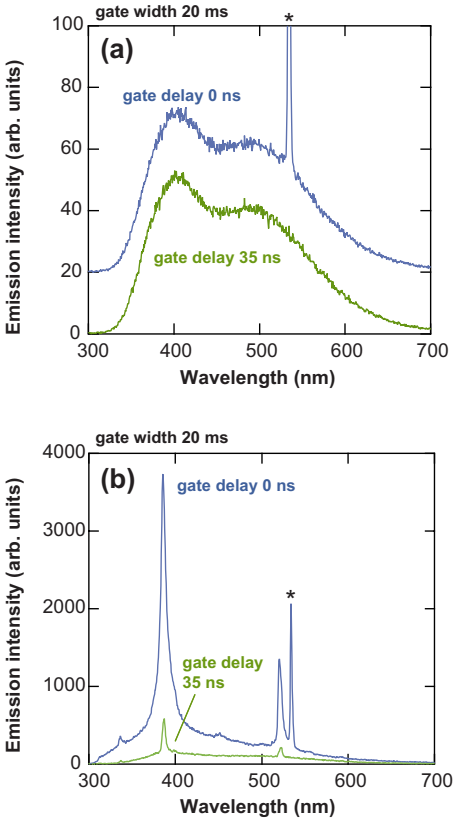

FIG. 7. (Color online) Time-resolved PL spectra of the MgO-only powders recorded under different pump fluences: (a) 10 mJ/cm^2 and (b) 210 mJ/cm^2. The gate delay times of the upper and lower spectra are 0 and 35 ns, respectively. All the spectra were recorded with a constant gate width of 20 ms. In (a), the upper spectrum is vertically shifted for clarity. Asterisk indicates the second harmonic (532 nm) of the Nd:YAG laser contaminated in the incident laser beam.

nature of the emissions above threshold can also be seen in alternative time-resolved measurements shown in Figs. 4 and 5. This substantial reduction in the decay time for the entire spectral region will provide another support for lasing. We should also note that the emission band still consists of a broad spectral component even above the lasing threshold, which is a general characteristic of color center lasers as mentioned in Sec, I.

IV. DISCUSSION

A. Mechanism of light amplification

If the laserlike emission from the colored MgO powder results from the total internal reflection of individual MgO particles, a similar optical amplification process is also expected to occur in the mixture of MgO and SiO_2. Figure 2, however, demonstrates that the threshold behavior of the emission intensity is observed solely from the MgO-only powder. This strongly indicates that the interparticle scattering in the gain MgO particles plays a vital role in the light-emission process. We hence suggest that the observed light amplification process results from random lasing, which is induced by multiple scattering in an amplifying disordered medium.[12] According to the multiple-scattering scheme,[12] the absence of light amplification in the MgO/SiO_2 mixture can be interpreted in terms of the absence of feedback supplied by the interparticle interactions among the colored MgO particles. That is, in the MgO/SiO_2 mixture the gain length l_g, which is defined as the path length over which the light intensity is amplified by a factor of e, will be infinitely long as a result of the coexistence of α-quartz particles, which will not contribute to any feedback or light amplification at all.

Recently, the interest in random lasing has increasingly grown since the observation of this phenomenon from powder phosphors of Nd-doped laser crystals.[13] Later experiments have further demonstrated that random laser action is observed in a variety of systems, for example, scattering microparticles in a laser dye solution[14–16] and aggregations of active semiconductor powders such as ZnO.[17,18] Although random laser action appears to be observed generally in amplifying disordered media,[19] the lasing characteristics, e.g., band width, decay time, and lasing threshold, are strongly dependent on the factors that can potentially affect the scattering process, such as particle size,[20] pulse width of the excitation laser,[21] and pumping beam diameter.[17,22] It is hence probable that the lasing behavior of the present colored MgO microcrystals may also be affected by the conditions for pumping and the particle characteristics. These experiments are now under way and the results will be reported in a forthcoming paper.

B. Origin of the peaks at 384 and 518 nm

As shown in Fig. 3, the sharp emission peaks at 384 and 518 nm were observed in both the MgO-only and the MgO/SiO_2 mixture powders for high-fluence excitation although light amplification was observed only from the former sample. In this section, we discuss a possible origin of these two sharp peaks in view of the optical excitation process of the F-type centers (F^+ and/or F centers).

Previously, it was reported that laser ablation of an MgO single crystal using a pulsed ultraviolet (UV) laser yields a fluorescent plume, showing several atomic emission lines related to Mg.[23,24] In particular, two dominant peaks can be found at ~383 and ~518 nm, which are attributed to transitions among triplet states in excited neutral Mg (Mg°), namely, $3d\ ^3D \rightarrow 3p\ ^3P$ and $4s\ ^3S \rightarrow 3p\ ^3P$, respectively.[23,24] We should note that the wavelengths of these Mg° line emissions are almost comparable to those of the two sharp peaks shown in Fig. 3. This suggests that the atomic emissions of Mg° tend to contribute to the emission spectra of the MgO-only powder as well as those of the MgO/SiO_2 mixture with increasing excitation fluence. We, however, consider that the origin of the sharp peaks reported here is not a laser-produced plasma or a corresponding fluorescence plume because plume fluorescence is preceded by laser ablation and is hence not observed below the laser damage threshold of a material.[25,26] As for MgO, the laser damage threshold is reported to be 2–3 J/cm^2,[23] which is far above the fluence employed in this work. Indeed, we did not observe any ap-

parent damage of the samples and the related plasma plume, which is normally found as a bright emission region extending to a distance of a few millimeters from a target,[26]

As an alternative to the usual laser-produced plasma scheme, we here present a model for the generation of Mg° line emissions in the colored MgO microcrystals in view of the photoionization of the *F*-type centers. This model is based on the experimental results on photodesorption of Mg ions from MgO crystals reported by Dickinson and co-workers.[27] These researchers[27] demonstrated that Mg ions, principally Mg^{+}, are photodesorbed from mechanically preabraded MgO single crystals under high vacuum ($\sim 10^{-7}$ Pa) by pulsed 248 nm excimer laser irradiation at fluences starting from ~ 20 mJ/cm^2, which are well below the damage or ablation threshold of MgO (2–3 J/cm^2). This photodesorption phenomenon was interpreted in terms of a strong Coulomb repulsion between the positively charged photoionized *F*-type centers and the surface Mg ions, accompanied by the following photoinduced charge exchange:[27]

$$F^{+}(\text{or } F) + Mg^{2+} + h\nu \rightarrow F^{2+}(\text{or } F^{+}) + Mg^{+}. \quad (1)$$

We propose that the above electrostatic model can also be applied to the present case. In their photodesorption experiments of Dickinson and co-workers,[27] any PL emissions related to Mg° and the *F*-type centers were not reported to be observed as long as the irradiation fluence is below the threshold of ablation. This is probably because the population of the *F*-type centers, which are supposed to be present only at the preabraded MgO surfaces, is quite low in their samples. In the present colored MgO microcrystals, however, a large number of *F*-type centers is likely to exist not only at the surface but also in the bulk. In our previous paper, the internal and external emission quantum yields are $11.2\% \pm 0.5\%$ and $5.1\% \pm 0.4\%$, respectively, implying large amounts of *F*-type centers are included in the MgO microcrystals. It is hence reasonable to expect that a substantial amount of Mg ions located near the *F*-type centers in the bulk can be "freed" (but will not be photodesorbed) under pulsed laser irradiation via a repulsive force from the photoionized *F*-type centers, similar to the case of Eq. (1).

In addition to the above process, the photoionization of the *F*-type centers will also generate free electrons as follows:[6]

$$F^{+}(\text{or } F) + h\nu \rightarrow F^{2+}(\text{or } F^{+}) + e^{-}. \quad (2)$$

As a result, the ionized state consisting of Mg^{+} ions and electrons is expected to be formed inside the colored MgO microcrystals. We should note, however, that this state is different from the usual laser-produced plasma since the present ionized state is not induced by the laser damage process but is created via the photoionization of the *F*-type centers well below the damage threshold. When such Mg^{+} ions and electrons coexist in the MgO crystals, it is probable that the Mg^{+} ions will recombine radiatively and/or collisionally with the electrons.[28,29] The former radiative recombination process will lead to the higher-lying neutral excited states and the subsequent Mg° line emissions as follows:

$$Mg^{+} + e^{-} \rightarrow Mg^{\circ *}, \quad (3)$$

$$Mg^{\circ *} \rightarrow Mg^{\circ} + h\nu'. \quad (4)$$

Thus, we propose that the radiative electron-ion recombination process initiated by the photoionization of *F*-type centers accounts for the origin of the observed 384 and 518 nm emissions.

The time-resolved PL measurements shown in Figs. 4 and 5 elucidated that the decay kinetics of the sharp peaks at 384 and 518 nm are hardly affected by the surrounding gas molecules although the peak width of the emissions tends to become broad slightly as a result of the presence of ambient gas molecules. This strongly implies that the expected radiative recombination process occurs mainly inside the microcrystals rather than at their surface. Figures 4 and 5 further demonstrated the following interesting features concerning the time dependence of the Mg° line emissions: (1) the decay time is on the order of ~ 20 ns (our instrumental resolution) when measured both in air and in vacuum, (2) the half width measured under vacuum is unchanged and has a constant value of ~ 6 nm during and after irradiation of ns laser pulse, and (3) the half width measured in air is broad (~ 20 nm) during pulsed laser irradiation and then becomes narrow (~ 8 nm) after ceasing the irradiation of laser pulse. The changes in the half width during and after pulsed laser irradiation observed in air can be interpreted in terms of the collisions of the ambient gas molecules. It should be noted, however, that as long as the measurements are carried out in vacuum, the half width remains narrow even in the course of the irradiation of ns laser pulse. This allows us to suggest that the density of excited electrons during the present pulsed laser irradiation will not be high enough to induce the Stark broadening, also indicating a less possibility of bottom-up excitations of the ground-state Mg° atoms by collisions of energetic electrons. It has been demonstrated that collisions of charged particles such as electrons and ions will exhibit the Stark broadening in the relevant emission spectra;[30] the full width at half maximum (FWHM, $\Delta\lambda_{1/2}$) of a Stark-broadened line without ionic contribution scales linearly with the electron density n_e as follows:[30]

$$\Delta\lambda_{1/2} = 2W(n_e/10^{16}), \quad (5)$$

where *W* is the electron-impact parameter which can be incorporated for different temperatures. If the excitation process is dominated by electron collisions, the FWHM $\Delta\lambda_{1/2}$ will show a temporal decrease because of an expected decrease in electron density with elapsing measuring time. As mentioned earlier, however, the half width of the sharp emission lines hardly changes as long as the measurements are carried out in vacuum, implying that the collision of energetic electrons does not play an important role in the present emission process. Furthermore, Figs. 4 and 5 show that the Mg° line emissions show rather a fast decay within the time scale of several tens of nanoseconds and that the decay profile is hardly affected by the pump fluence. These observations appear to be inconsistent with the bottom-up excitation process due to collisions of energetic electrons as well; rather the observed fast decay feature implies a stimulated emission process for both the F^{+}-center and the Mg° line emissions. After the recombination and emission processes, electron

transfer from the ground-state Mg° atoms to the photoionized *F*-type centers will eventually occur and accordingly the Mg ions and the *F*-type centers will return to the original structural and electronic states in the crystal lattice.

According to the above scheme, the onset of the Mg° line emissions is not necessarily related to interparticle scattering processes but will be inherent to the photoexcitation process of the individual colored MgO particles, explaining the reason why the 384 and 518 nm peaks can be found in both the MgO-only and the MgO/SiO_2 mixture powders. However, the light amplification resulting from multiple-light scattering is realized exclusively in the MgO-only powders, as mentioned repeatedly in this paper.

In our previous paper,[10] we assumed that the appearance of the several sharp peaks, such as those at 384 and 518 nm, in the emission spectra of the MgO microcrystals shows one piece of evidence of laser action. However, provided that the sharp peaks at 384 and 518 nm are attributed to atomic emissions of Mg°, the appearance of these sharp peaks does not simply indicate the occurrence of laser emissions. Instead, the existence of optical gain shown in Fig. 6 newly presents a more direct piece of evidence of stimulated emission from the colored MgO microcrystals.

V. SUMMARY

We have demonstrated that the laserlike emission reported recently from the colored MgO microcrystals was not observed from the MgO/SiO_2 mixture powder, suggesting that the light amplification process results from random lasing or the multiple scattering with gain in the colored MgO particles. We have also demonstrated from pump-probe measurements that optical gain of a probe beam is observed, further corroborating the existence of stimulated emission. The sharp emission lines at 384 and 518 nm, which are found to occur in both the MgO-only and the MgO/SiO_2 mixture samples under high-fluence excitation, result from the Mg° line emissions in the absence of the usual laser-produced plasma. In the colored MgO microcrystals the Mg° line emissions will arise via the photoionization of the *F*-type centers [Eqs. (1) and (2)], followed by electron-ion recombination [Eq. (3)] and radiative de-excitation [Eq. (4)]. The decay kinetics of the sharp peaks at 384 and 518 nm were found to be hardly affected by the surrounding gas molecules although the peak width of the emissions tends to show a slight broadening as a result of the presence of ambient gas molecules. It is hence probable that the expected radiative recombination process occurs mainly inside the microcrystals rather than at their surface. Furthermore, we infer from the time-resolved PL measurements that not only the sharp peaks at 384 and 518 nm but also the broad F^+-center emission exhibit a fast decay within the time scale of several tens of nanoseconds above the threshold fluence, suggesting that both the F^+ center and the Mg° emissions are responsible for lasing.

Thus, the present results have elucidated that the color centers embedded in microcrystals can dramatically modify the electronic and optical processes in MgO, hence attracting renewed and extended interest in the color centers in wide band-gap materials.

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