

Controls and Constructive Applications of Defects
in Local Area of Oxides
Using Femtosecond Laser

Chiwon Moon

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General Introduction

The behavior of defects in a single crystal such as pores, cracks, and dislocations has been the subject of considerable interest for decades since it is directly related to the mechanical, electrical properties, and durability of the materials. In particular, the defects in sapphire have been widely investigated because the crystal is one of the most commonly-used materials in many applications, involving a substrate for semiconductor devices, a solid-state laser medium, high-durability windows, artificial bones and so on which are attributable to its remarkable hardness and strength. The defects resulting from a deformation of sapphire have been well studied concerning with fracture, crack, and dislocation. In studies of defects in sapphire, several methods have been proposed to introduce defects into sapphire.

The most common methods include indentation, impact, and abrasion. The behavior of surface deformation has been studied using these methods. Someone reported the formation of dislocations at the surface of sapphire due to the abrasion or polish. Nowak et al. discussed the anisotropic surface deformation and fracture of sapphire using triangular and spherical indenter for different crystallographic planes of sapphire.^{1; 2} However, these methods are limited to create defects only at the surface of solids. Compression methods can introduce cracks inside sapphire as well as dislocations. Nakamura et al. deformed a sapphire bulk crystal with a constant strain-rate using “two-stage deformation” technique consisting of deformation at 1400°C as the first stage, and additional deformation at 1200°C as the second stage and they introduced dislocations inside sapphire.³ However, the distribution of the dislocations is random and the experimental procedures require high temperature above 1200°C. On the other hand, ion beam etching combined with a crystal bonding allows the introduction of controlled defect structures at the interface of sapphire, and J. Rödel et al.

studied healing behavior of cracks inside sapphire at 1800°C using this method.⁴⁻⁶ The sample preparation procedure of ion beam etching method consists of successive sequences of photoresist coating, UV radiation, etching, unetching, and bonding. However, this lithographic patterning method requires a complex procedure for sample preparation. Also such defect structures are typically in the micrometer size, and the defects are formed not inside but on the surface at first. Hence, to control and evaluate the nanometer-scale defects introduced truly inside sapphire is one of the important problems.

Here, we used femtosecond laser for introducing controlled nanometer-scale defects inside sapphire. Femtosecond laser is one of the pulsed laser that emits ultrashort optical pulses that have a pulse width with femtosecond (10^{-15} second) range. Femtosecond laser is superior to modify an internal area of transparent materials as compared to other pulse lasers having pulse duration beyond one picosecond. First, since the pulses is compressed and emitted for ultrashort time, it is possible to gain large peak intensity with same pulse. Second, tightly focused femtosecond laser can induce nonlinear absorption of light in transparent material leading to change of material properties at the focal volume. Third, short pulses require less energy than longer pulses to reach the threshold for optical breakdown. Decreasing the photon energy leads to more precise processing or material modification.

Damage mechanism using femtosecond laser pulses is fundamentally different from that of another such as picosecond or nanosecond laser. The laser wavelengths of pulse lasers having a pulse width of nanosecond or longer duration are usually in the ultraviolet regions, therefore, interactions between light - materials occur at the surface of the material. For pulse durations longer than a few tens of picoseconds, the energy is transferred from the laser-excited electrons to the lattice on the time scale of the pulse duration. This energy is then

carried out of the focal volume by thermal diffusion. Damage occurs when the temperature of the material in the irradiated region reaches high enough for the material to melt or fracture.⁷

On the other hand, when a femtosecond laser pulse with high peak intensity is focused into a microscopic area of transparent material, nonlinear photoionization occurs at the focal point.^{7;}

⁸Photoionization refers to direct excitation of the electron by the laser field. There are two schemes of photoionization, the multiphoton ionization and the tunneling ionization depending on the frequency and intensity of the laser. For strong laser fields and low laser frequency, the tunneling ionization is dominant; the Coulomb well is suppressed enough that a valence electron tunnels through the barrier and becomes free. At high laser frequencies, multiphoton absorption occurs which indicates that an electron absorbs several photons simultaneously. A single photon of visible light does not have enough energy to excite an electron in a transparent material from the valence to the conduction band. However, the electron can be promoted from the valence to the conduction band when the number of photons absorbed times the photon energy is equal to or greater than the band-gap of the material, even though the wavelength of excitation does not agree with that of absorption region of the material.

Once a free electron in the conduction band is produced, it become a ‘seed’ electron that can absorb photons through inverse Bremsstrahlung absorption and gains energy during the process. After a sequence of several inverse Bremsstrahlung absorption processes, the kinetic energy is sufficiently large to collisionally ionize another electron from the valence band.⁹⁻

¹¹Then, two electrons are ready to gain energy through inverse Bremsstrahlung absorption, and the repeating sequence of the inverse Bremsstrahlung absorption and collisional ionization results in an avalanche growth in the number of free electrons. This process is called ‘avalanche ionization’.¹² Because, a time scale of photon absorption by an electron is

shorter than that of energy transfer to the lattice and lattice heating processes, free electrons promoted from valence to the conduction band by the nonlinear excitation are further heated by the laser pulse much faster rather than the speed they can cool by phonon emission. The density of the nonlinearly excited electrons grows through avalanche ionization until the excited electrons gain enough energy to excite other bound electrons.

When the excited electrons acquire the critical density, they behave as plasma having the resonant frequency of the incident laser. Because the presence of plasma results in a decrease in the refractive index, most of the laser energy is absorbed.^{13; 14} After the laser pulse is gone, the energy is transferred from the electrons to the lattice. A short time scale of energy deposition suppresses heat diffusion out of the focal point area. As a result of the tight focusing and nonlinear absorption process, a phase or structural modification occurs only in selective internal area, resulting in permanent change in the properties of materials without surface damages.¹⁵ Depending on the laser irradiation condition, cracking, pore formation or localized melting occurs. Furthermore, the modified area after laser irradiation often shows a permanent change in a size range down to the nanometer, which is smaller than the laser wavelength. For example, there are several reports on the capabilities for the subwavelength processing of femtosecond laser involving the alignment of periodic nanometer-scale grating in glass, cross patterning based on local dislocations, and the formation of nano-rods on silicon.¹⁶⁻¹⁸

In this research, we utilized femtosecond laser for micro processing an internal area of sapphire. We introduced nanometer-scale defects inside sapphire using focused femtosecond laser pulses and investigated the behaviors of the defect formation. After laser irradiation, we examined the effect of the heat treatment on the defect structures induced by laser irradiation. The morphological changes of the defect structures after the annealing and its mechanism are

discussed. Also, we aim for the fabrication of two-dimensional nanometer-scale structures inside sapphire which have unique behaviors as compared with bulk sapphire. These and related phenomena are discussed in the following chapters.

Chapter 1: The concept of femtosecond laser, a new regime of light – matter interactions are reviewed. The current state and future perspective of the femtosecond laser applications and efforts in the development of new materials are described.

Chapter 2: This chapter provides the behaviors of defects formed inside the local volume of sapphire by femtosecond laser irradiation. Specific defect structures at the focal point were analyzed using optical microscope and transmission electron microscope (TEM), and the origin of the defect structures were discussed in terms of the crystal structure of sapphire. The relation between the size of defect structures and the irradiation conditions was investigated.

Chapter 3: This chapter provides morphological investigation of the induced defect structures after the heat treatment subsequent to the femtosecond laser irradiation. The behaviors were evaluated by changes of defect structure inside sapphire are presented. In addition, the thermal effects on crystallinity and residual strain at the focal point were evaluated.

Chapter 4: This chapter provides long - lasting phosphorescence (LLP) properties of oxygen defect combined with cations in perovskite oxide. The lifetime of phosphorescence was presented which was calculated from the obtained decay curve. The origins of the luminescence center and electron trap were discussed concerning with the defects using electron spin resonance (ESR). The mechanism of LLP was also presented.

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Chapter 1

Introduction of Femtosecond laser

1.1. Fundamental on Femtosecond Time Scale

A femtosecond laser is a laser which emits optical pulses with a duration well below 1 picosecond ($1\text{ps} = 10^{-12}\text{s}$), i.e., in the domain of femtosecond. One femtosecond is the $1 : 10^{15}$ th part of a second and corresponds to about half a period of red light. The ratio of one femtosecond to one second is about the ratio of five minutes to the age of the earth. During one femtosecond, visible light travels over a distance of several hundred nanometers, which is quite a remarkable number of atomic distances. This suggests the importance the femtosecond time scale might have in the microcosm. Indeed, various essential processes in atoms and molecules as well as interactions among them, proceed faster than what can be resolved on a picosecond time scale. Their relevance results simply from the fact that these events are primary steps for most reactions in physics, chemistry and biology. An atom in a excited state is expected to show some macroscopic properties changing periodically on a femtosecond time scale. For the chemical reaction such as $(\text{AB})^* \rightarrow \text{A} + \text{B}$, the breaking of the bond is accompanied by a geometrical separation of the two components caused by a repulsive potential. The transition from the bound state to the isolated complexes proceeds within 100 femtosecond. Considering a solid where the atomic particles are usually trapped at a relatively well-defined position in the lattice, their motion is restricted usually to lattice vibrations (phonons) with possible periods in the order of 100 femtosecond. The fundamental problem to be solved is to find tools and techniques which allow us to observe and manipulate on a femtosecond time scale.

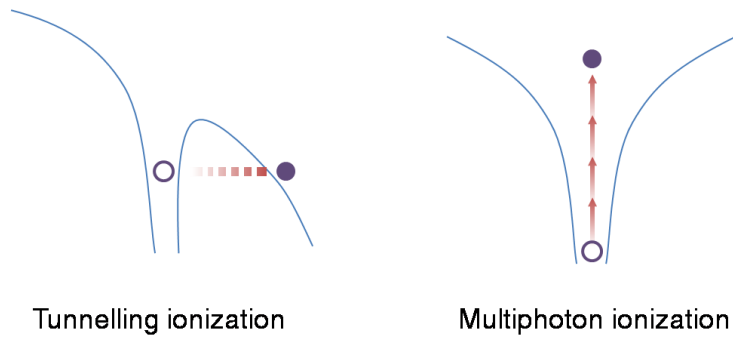
The time scale of a femtosecond becomes accessible due to progress in the generation, amplification and measurement of ultrashort light pulses. Femtosecond technology opens up new fascinating possibilities based on the unique properties of femtosecond pulses. Large energy can be concentrated in a temporal interval as short as several femtoseconds which corresponds to only a few optical cycle in the visible range. The pulse peak power can be extremely large even at modulate pulse energies. For example, a 50 femtosecond pulse with an energy of 1 mJ exhibits a peak power of 20 Gigawatt. Focusing this pulse to a $100\text{ }\mu\text{m}^2$ spot yields an intensity of 20 Petawatt / cm^2 . The geometrical length of a femtosecond pulse amounts only to several micrometer. In particular, the availability of femtosecond pulse allows materials to be subjected to a higher laser intensity than ever before, opening the door to the study of laser – material interactions in a new regime. Fundamental mechanisms responsible for the light – matter reaction in the time scale of a femtosecond will be discussed in the next section.

1.2. Nonlinear Interaction of Light with Matter

Femtosecond laser results in the laser-induced optical breakdown, a process by which optical energy is transferred to the material, ionizing a large number of electrons that transfer energy to the lattice. As a result of the irradiation, the material can undergo a phase of structural modification, leaving behind a localized permanent change in the refractive index or even a void. The absorption of light in a transparent material must be nonlinear because there are no allowed electronic transitions at the energy of the incident photon ¹. For such nonlinear absorption to occur, the electric-field strength in the laser pulse must be approximately equal to the electric field that binds the valence electrons in the atoms - of the order of 10^9 V m^{-1} , corresponding to a laser intensity of $5 \times 10^{20} \text{ W m}^{-2}$. To achieve such electric-field strengths with a laser pulse, high intensities and tight focusing are required. For example, a 1- μJ , 100-fs laser pulse must be focused to a $200\text{-}\mu\text{m}^2$ area. The tight focusing and the nonlinear nature of the absorption make it possible to confine the absorption to the focal volume inside the bulk of the material without causing absorption at the surface, yielding micromachined volumes as small as $0.008 \mu\text{m}^3$ ².

During irradiation, the laser pulse transfers energy to the electrons through nonlinear ionization ^{1;3}. Because a single photon of visible light does not have enough energy to excite an electron in a transparent material from the valence to the conduction band, multiple photons are required to excite the electron. Depending on the laser frequency and intensity, there are two different regimes of photoionization, the multiphoton ionization regime and the tunnelling ionization regime. Keldysh showed that both multiphoton and tunnelling regimes could be described within the same framework ⁴. The conceptual picture and the approximations used in calculations for these two mechanisms are very different, however.

(a)



(b)

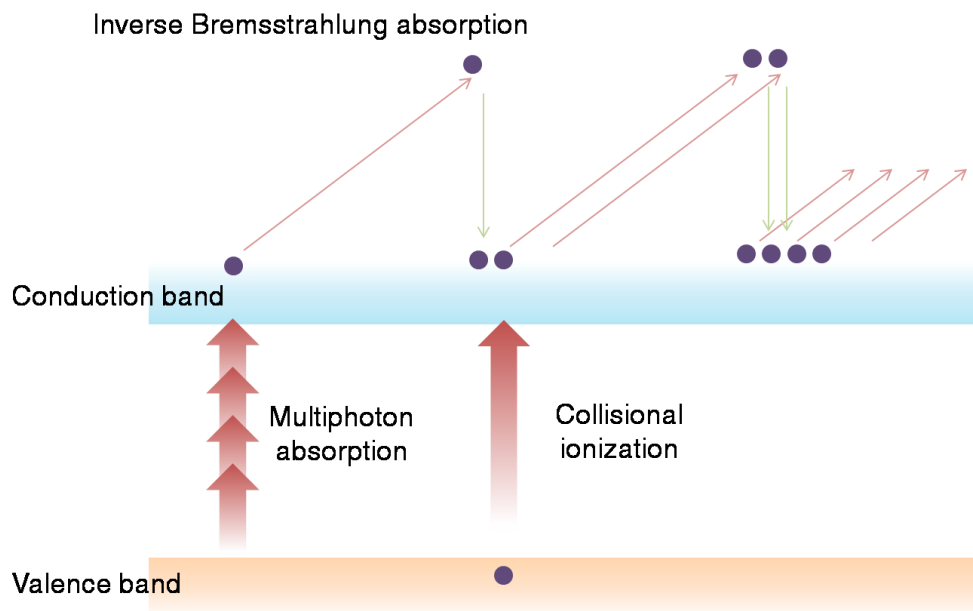


Figure 1.1 Schematic diagram of (a) the photoionization of an electron, (b) avalanche ionization which shows an interplay of photoionization, inverse Bremsstrahlung absorption, and collisional ionization.

In tunnelling ionization, the electric field of the laser suppresses the Coulomb well that binds a valence electron to its parent atom. If the electric field is very strong, the Coulomb well can be suppressed enough that the bound electron tunnels through the short barrier and becomes free, as shown schematically in the left-hand panel of figure 1.1(a). This type of nonlinear ionization dominates for strong laser fields and low laser frequency.

At high laser frequencies, nonlinear ionization occurs due to the simultaneous absorption of several photons by an electron, as shown in the right-hand panel of figure 1.1(a). To be promoted from the valence to the conduction band by this multiphoton absorption, the electron must absorb enough photons so that the number of photons absorbed times the photon energy is equal to or greater than the band-gap of the material.

For pulse durations greater than 10 femtosecond, the nonlinearly excited electrons are further excited through phonon-mediated linear absorption, until they acquire enough kinetic energy to excite other bound electrons - a process called avalanche ionization. Avalanche ionization involves free-carrier absorption followed by impact ionization. An electron already in the conduction band of the material linearly absorbs several laser photons sequentially, moving to higher energy states in the conduction band, so-called inverse Bremsstrahlung absorption as illustrated in Fig. 1.1(b). In order to conserve both energy and momentum, the electron must transfer momentum by absorbing or emitting a phonon or scattering off an impurity when it absorbs a laser photon. For electrons high in the conduction band, the deformation potential scattering time is approximately 1 femtosecond, so frequent collisions make free carrier absorption efficient ⁵. After the sequential absorption of n photons, the electron's energy exceeds the conduction band minimum by more than the band-gap energy, where n is the smallest number which satisfies the relation $n\hbar\omega \geq E_g$, and ω is the laser frequency, E_g is the band-gap of the material. The electron can then collisionally ionize

another electron from the valence band, as illustrated ‘collisional ionization’ in Fig. 1.1(b). The result of the collisional ionization is two electrons near the conduction band minimum, each of which can absorb energy through free-carrier absorption and subsequently impact ionize additional valence band electrons. As long as the laser field is present, the electron density, N , in the conduction band grows according to

$$\frac{dN}{dt} = \eta N$$

where η is the avalanche ionization rate.

Avalanche ionization requires some ‘seed’ electrons in the conduction band of the material. These initial electrons are provided either by thermally excited carriers, by easily ionized impurity or defect states, or by carriers that are directly photo-excited by multiphoton or tunnelling ionization. When the density of excited electrons reaches about 10^{29} m^{-3} , the electrons behave as a plasma with a natural frequency that is resonant with the laser - leading to reflection and absorption of the remaining pulse energy⁶.

1.3. Damage mechanisms of Interactions between Light and Matter

Figure 1.2 shows the timescales for a number of relevant physical processes involved in femtosecond laser micromachining. Part of the optical energy absorbed by the electrons is transferred to the lattice over a picosecond timescale. Within a couple of nanoseconds, a pressure or a shock wave separates from the dense, hot focal volume⁷⁻⁹. On the microsecond timescale, the thermal energy diffuses out of the focal volume. At a sufficiently high energy these processes cause melting or non-thermal ionic motion and leave behind permanent structural changes¹⁰.

Laser-induced damage has been studied since the early days of the laser⁵, but damage caused by femtosecond laser pulses is fundamentally different from damage caused by laser pulses with a duration greater than one picosecond.

For pulse durations longer than a few tens of picoseconds, energy is transferred from the laser-excited electrons to the lattice on the time scale of the pulse duration. This energy is then carried out of the focal volume by thermal diffusion. Damage occurs when the temperature of the material in the irradiated region becomes high enough for the material to melt or fracture¹¹. Energy is deposited into the material by the laser pulse and is transported out of the irradiated region by thermal diffusion, thus it is the relative rate of energy deposition and thermal diffusion that determines the damage threshold. Simple calculations show that, in this case, the threshold fluence for optical damage scales as the square root of the pulse duration.

For damage caused by pulses longer than a few tens of picoseconds, the source of the initial conduction-band electrons that seed the avalanche ionization is very important. Avalanche ionization is very efficient for such pulses because the long pulse duration allows

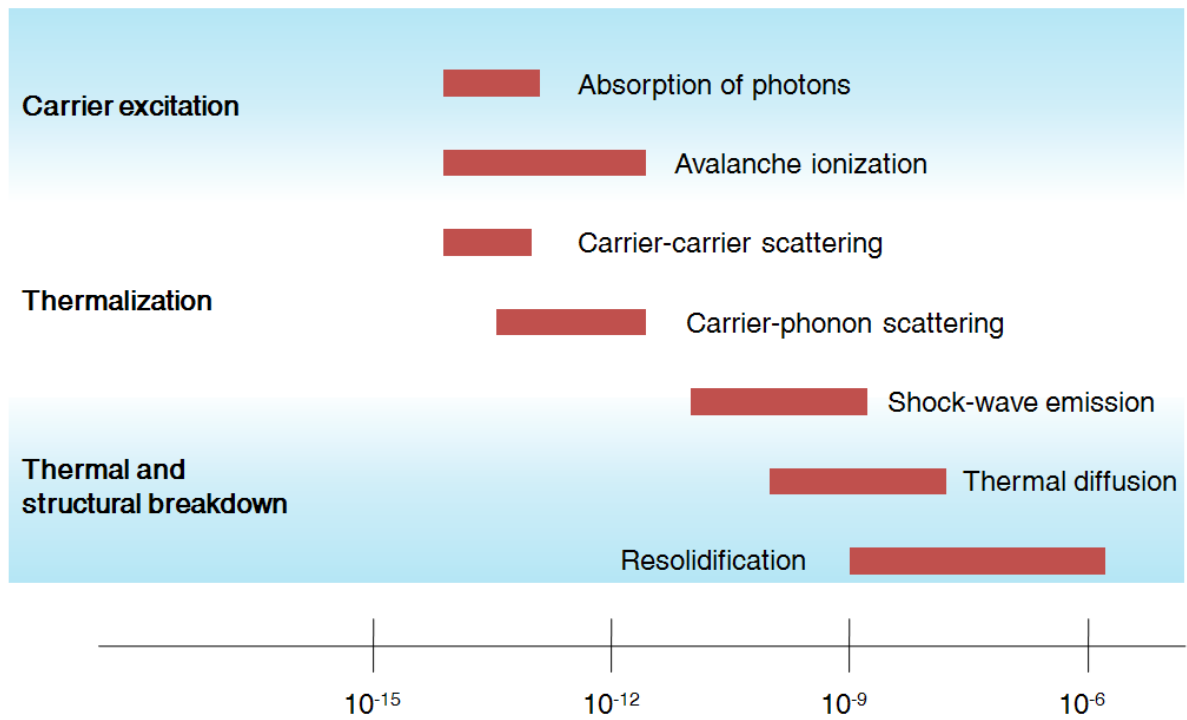


Figure 1.2. Timescale of the physical phenomena associated with the interaction of a femtosecond laser pulse with transparent materials.

more time for exponential growth of the electron density. Because avalanche ionization is so efficient, the laser intensity required to produce damage is not high enough to directly photoionizing electrons, so either thermally excited electrons or impurity and defect states provide the initial seed electrons for the avalanche. A high concentration of easily ionized impurity electrons lowers the threshold for optical damage compared to that of the pure material, making determination of the intrinsic breakdown threshold difficult ¹².

For pulses shorter than a few picoseconds, the mechanism for optical damage is simpler than for longer laser pulses. Absorption occurs on a time scale that is short compared to the time scale for energy transfer to the lattice, decoupling the absorption and lattice heating processes ³. Electrons in the conduction band are heated by the laser pulse much faster than they can cool by phonon emission. The electron density grows through avalanche ionization until the plasma frequency approaches the frequency of the incident laser radiation (the ‘critical’ plasma density) ³. This high density plasma strongly absorbs laser energy by free-carrier absorption. The reflectivity of the plasma at the critical density is only a few percent, so most of the laser energy is transmitted into the plasma where it can be absorbed. At higher plasma densities, however, a significant fraction of the laser pulse energy can be reflected. Only after the laser pulse is gone is energy transferred from the electrons to the lattice. This shock-like deposition of energy, on a time scale much shorter than the thermal diffusion time, leads to ablation of material on the surface or permanent structural change in the bulk.

For sub-picosecond laser pulses, photoionization plays an important role in the generation of conduction band electrons. Photoionization by the leading edge of the laser pulse provides the seed electrons for avalanche ionization during the rest of the pulse ³. This self-seeded avalanche makes short-pulse breakdown less dependent on defects in the material than long-pulse breakdown and therefore the threshold for short-pulse damage is deterministic ¹². For

very short laser pulses, photoionization can dominate avalanche ionization and produce a sufficient plasma density to cause damage by itself^{3; 13}.

Damage produced by pulses in the femtosecond range is far more regular from shot to shot and more confined than with longer pulses². Because short pulses require less energy than longer pulses to reach the intensity necessary to produce optical breakdown, they deposit less energy in the material. Less energy deposition leads to more precise ablation or bulk material modification. This deterministic breakdown and damage near threshold and controllable material alteration make femtosecond lasers an ideal tool for micromachining¹⁴.

1.4. Innovative Applications of Femtosecond Laser

Femtosecond has been used to fabricate photonic devices using a variety of transparent substrates, including glasses, crystals and polymers. Owing to their high purity and large transparency, window, glasses and crystals are commonly used as base materials. A wide variety of femtosecond-laser micromachined devices have been demonstrated using glasses and crystals, including waveguides, active devices, filters and resonators. The use of transparent polymers as a substrate material for fabrication presents advantages over other transparent materials. First, polymers are also an attractive medium owing to the ease with which dopants can be incorporated into them, the diversity of available compositions and physical properties, and their low cost. However, compared with glasses and crystals, polymers have higher transmission losses. So far only a few photonic devices have been directly fabricated in polymers, such as ring-mode ¹⁵ and single-mode ¹⁶ waveguides in polymethylmethacrylate.

Along with data storage ², waveguide fabrication was one of the first demonstrations of the potential of femtosecond laser micromachining for photonic applications ^{17; 18}. Femtosecond laser micro-machined waveguides can serve as interconnects in a variety of host glasses, and have opened up the possibility of three-dimensional layering of waveguides. The pulse energy required for fabricating devices can be as low as a few nanojoules, requiring only a laser oscillator ^{19; 20}.

Over the past decade, the transmission losses, refractive-index contrast and bending radii of femtosecond-laser-micromachined interconnects have been characterized. The spatial profile of the refractive index of waveguides is strongly dependent on the material and the processing conditions ^{17; 19; 21; 22}, and is close to that of a fibre for fused silica substrates ²³. Additionally, minimum bending radii of the order of tens of millimeters have been achieved

²⁴. Photonic-circuit designs might require micromachining interconnects across several substrates. Optically connected waveguides have already been fabricated in bonded doped and undoped phosphate glass, and also through multiple pieces of glass separated by air gaps.

The intrinsic nonlinear spatial confinement of femtosecond laser microfabrication can be used not only to process cured polymers, but also to induce polymerization in a resin. Usually referred to as two-photon polymerization ²⁵, or laser direct writing ²⁶, this polymerization technique makes it possible to fabricate polymer structures with a high degree of complexity. Many interesting optical applications of two-photon polymerization exist, most notably three-dimensional photonic crystals ²⁷. Two-photon polymerization is a large field with applications far exceeding the domain of photonics.

The controlled delivery of thermal energy during femtosecond laser micromachining can be used for material processing. Bonding of dissimilar materials is an engineering challenge because the mismatch between thermal expansion coefficients causes thermo–mechanical stress at the joint, weakening the bond ²⁸. Also, bonding two transparent materials requires an additional, partially opaque intermediate layer ²⁸. Femtosecond laser processing based on nonlinear absorption overcomes the need for this intermediate layer, and the rapid cooling strengthens the bond.

Femtosecond lasers can also be used to induce spatially selective phase transitions within a material. For example, crystals can be grown inside a piece of glass by exposing it to a series of femtosecond pulses ²⁹. The laser pulses heat the glass in the focal volume beyond the melting point, acting as a localized source of heat. Once a seed crystal is formed, the repeated heating and cooling causes these seed crystals to grow. This technique for inducing phase transitions can also be used for data-storage applications. For example, when samarium ions

embedded in a glass host are irradiated with a femtosecond laser pulse, a transition from Sm^{3+} to Sm^{2+} is induced³⁰. The exposed ions fluoresce at a different wavelength from the unexposed ions, and so each exposed area can act as a data-storage bit.

1.5. Conclusion

Femtosecond laser presents unique capabilities for three-dimensional, material-independent, subwavelength processing. It enables the fabrication of three-dimensional photonic devices with far greater ease than lithography, and the field is maturing at an extraordinary pace. Because femtosecond laser micromachining also holds great promise beyond the field of photonics, it is a technology that creates new markets for the laser industry and enables innovative applications.

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Chapter 2

Introduction of Nanometer-Scale Cracks to Sapphire and Control of crack morphology using Femtosecond Laser

2.1. Introduction

Femtosecond lasers have attracted considerable attention because they can focus a large amount of energy on a microscopic area in various materials without causing surface damage. Femtosecond lasers are widely used in materials microprocessing when high accuracy and a small-sized structure are required. In particular, they have been applied to the fabrication of three-dimensional structures within various types of glass.¹⁻³

Recently, our group succeeded in fabricating and controlling a dislocation within an MgO single crystal by using femtosecond laser irradiation. The cross-shaped dislocation resulted from the interaction between laser pulses and an MgO single crystal with a rock-salt-type structure. Studies of the interaction between laser pulses and other single crystals have also been reported, including the amorphization of sapphire, refractive index change in an LiNbO₃ single crystal, and phase transformation of a TiO₂ single crystal.

Sapphire has a corundum structure and it has been used in abrasives and bearings because of its superior mechanical properties such as high melting point, high hardness, and low reactivity. In addition, sapphire is well known as a solid-state laser element when doped with transition metal ions such as Cr⁴ and Ti⁵. In the last decade, the mechanical properties of sapphire have mainly been investigated in terms of the deformation mechanism. For instance, dislocation, twinning, and cracks of sapphire have been studied by using the indentation and uniaxial compression methods.⁶⁻¹¹ However, there have been few reports on the relationship

between the crystal structure and the deformation mechanism by using laser irradiation.

In this chapter, we discuss the deformation mechanism in a microscopic damaged area of a ruby single crystal formed by femtosecond laser irradiation. Ruby is an appropriate material for this structural investigation because it has good transparency at the wavelength of the laser and an approximately linear pressure dependence of a sharp fluorescence R1 line at 694.2 nm at room temperature. Therefore, we can precisely evaluate the residual stress around the photomodified area from the emission peak shift.¹² We examine the deformation behavior after femtosecond laser irradiation in detail using an optical polarizing microscope, confocal Raman microscope, and transmission electron microscope (TEM).

2.2. Nanometer-Scale Crack Formation inside sapphire by Femtosecond Laser Irradiation

2.2.1. Experimentals

We used commercially available ruby (0.5 wt% Cr^{3+} doped) with dimensions of $5 \times 5 \times 1 \text{ mm}^3$ as a sample for laser irradiation. A femtosecond laser having a pulse width, wavelength, and repetition rate of 238 fs, 780 nm, and 1 kHz, respectively, was used as the optical source (IFRIT, Cyber laser). The pulse energy and number of pulses at the sample location were controlled by a neutral density (ND) filter and fast electronic shutter, respectively. A laser beam with a diameter of 5 mm in Gaussian mode was focused at a depth of 50 μm from the sample surface using a microscope objective lens (Nikon, 100x) with a numerical aperture (NA) of 0.9. The incident laser beam was normal to the $(11\bar{2}0)$ plane of the sample. To estimate the magnitude of residual stress around the focal point, we measured the fluorescence spectra of the photomodified area in a ruby sample excited by a Nd:YAG laser with a wavelength of 532 nm using microscopic Raman spectroscopy (Nanofinder® 30, Tokyo Instruments). The spatial and spectral resolution of the Raman microscope (100x objective, NA = 0.9) is approximately 275 nm and 0.98 nm, respectively. The three-dimensional structure at the photomodified area and the distribution of residual stress were observed using a polarizing microscope (Axio imager, Carl Zeiss) and TEM (JEOL 2010HC, 200kV). The TEM sample is prepared by a standard procedure using the ion-thinning method.

2.2.2 Results and Discussions

Figure 2.1 shows a low-magnification TEM image of the photomodified area in the sapphire sample after laser irradiation. The sample was irradiated with 1000 laser pulses having a pulse energy of 3 μJ . The center area of the focal point having a diameter of approximately 2 μm was extremely deformed by laser irradiation. In addition, cracks were formed around the focal point, which were curved at few site but generally straight, and they had uniform morphology at every focal point.

Figure 2.2(a) and (b) shows a bright-field TEM image of the photomodified area and electron diffraction pattern at the center area of the focal point, respectively. The deformed area comprised an amorphous phase in the middle, and polycrystals and dislocations in the edge. The phase transformation from a crystalline phase to an amorphous phase was due to the rapid heating and quenching by laser irradiation.^{13; 14} (ref Moon) A part of the polycrystals was mingled with the amorphous phase and they were scattered on the amorphorized area as single-crystal particles. In addition, we found that cracks were formed on the $(1\bar{1}02)$ and the $(1\bar{1}00)$ planes and they had a width of approximately 30 nm. The morphology of the cracks will be discussed later.

Figure 2.3 shows a top-view optical microscope photograph of the photomodified area in the $(11\bar{2}0)$ ruby sample irradiated with focused femtosecond laser beam with respect to the pulse energies of (a) 5, (b) 10, (c) 15, and (d) 20 μJ , respectively. The cracks were observed only along the $\{1\bar{1}02\}$ planes at the pulse energy of 5 μJ , however, the cracks on $\{1\bar{1}00\}$ planes became visible as the pulse energy increased, indicating that the cracks on $\{1\bar{1}02\}$ plane were formed in advance at the photomodified area than those on $\{1\bar{1}00\}$. It has been reported that

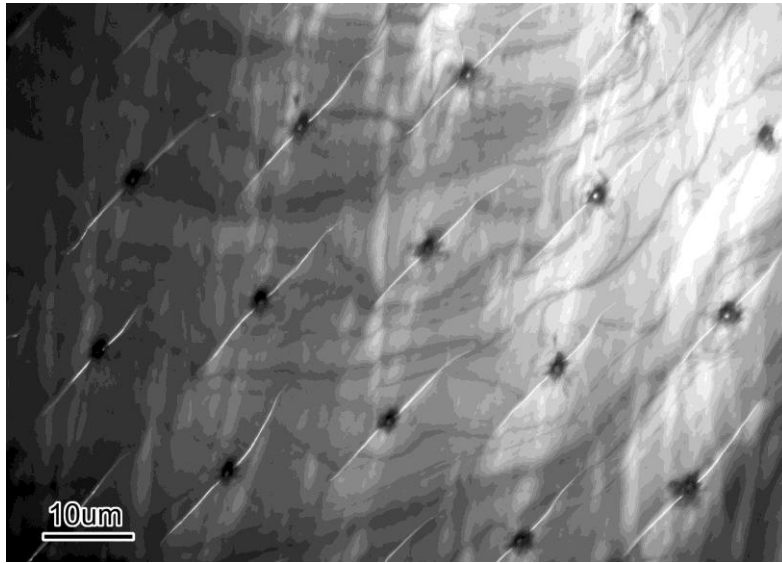


Figure 2.1 a low-magnification TEM image of sapphire after femtosecond laser irradiation with 1000 laser pulses of 3 μ J pulse energy

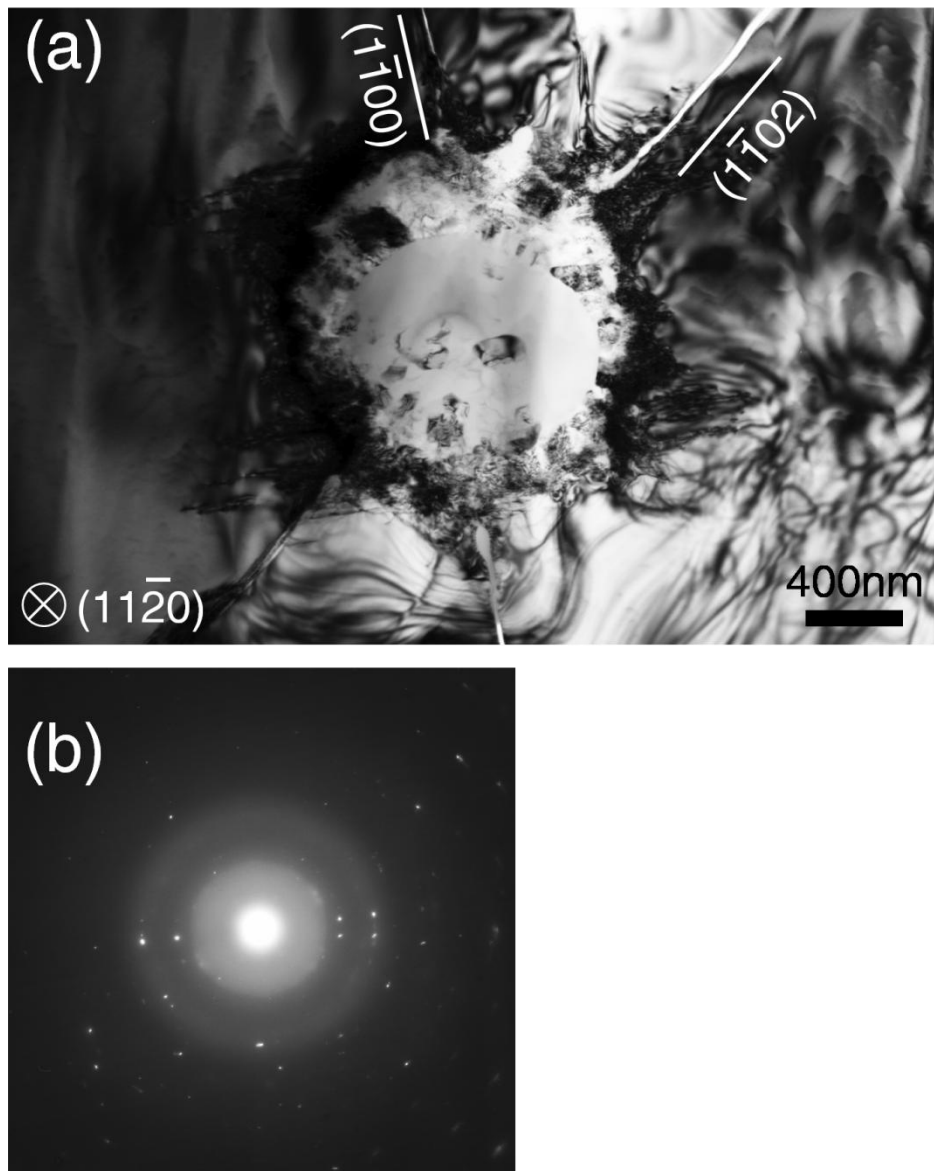


Figure 2.2 (a) Bright-field TEM image of the focal point. The bars indicate the crystallographic orientations of $(1\bar{1}02)$ and the $(1\bar{1}00)$ planes, respectively. (b) electron diffraction pattern obtained at the center of the focal point, indicating that an amorphous phase and single crystalline phase existed at the same time.

the fracture surface energies of the $\{1\bar{1}02\}$ and the $\{1\bar{1}00\}$ planes are 7.3 and 6.0 J/m², respectively, and they are low as compared to those of other low-index crystallographic planes as shown in Table 2.1, that is, these planes can be a preferential fracture path.¹⁵ Therefore, we estimate that the energy of the laser pulse preferentially initiate the cracks on the $\{1\bar{1}02\}$ and the $\{1\bar{1}00\}$ planes reflecting the crystallography of the sapphire crystal structure. (ref Moon) Consequently, the difference of the fracture surface energy between $\{1\bar{1}02\}$ and $\{1\bar{1}00\}$ planes is responsible for the sequence of the crack formation by laser irradiation. In addition, the angle between two cracks on $\{1\bar{1}02\}$ plane, α and β , is about 84.5° as shown in Fig 2.3 (e), which is averaged from 15 samples.

Figure 2.4(a) shows a side-view of optical microscope photograph at the photomodified area. The sample was irradiated with 1000 laser pulses having a pulse energy of 10 μ J. The photomodified area was 65 μ m long and has an elongated shape, and it was parallel to the direction of the laser beam. The dark area around the focal point was attributable to the light scattering by the cracks. In addition, the black dots were discretely aligned along the center of photomodified area. The formation of the periodic structures was due to the self-focusing process of femtosecond laser pulses which indicated the peak intensity enhancement of laser pulses induced by the change in refractive index of materials. The details of the black dots is discussed in the next chapter. Figure 2.4(b) shows top-view optical microscope photos at the corresponding depths as denoted in Fig. 2.4(a). The shape of the patterns changed with increasing depth from the focal point. The cracks on $\{1\bar{1}02\}$ planes were observed regardless of the depth. In contrast, the cracks on $\{1\bar{1}00\}$ planes were observed in the depths from focal

Fracture Plane	Fracture surface energy (J/m ²)	Comments
(0001)	>40	
{11 $\bar{1}$ 00}	7.3	25°C
{11 $\bar{1}$ 02}	6	25°C
{1 $\bar{1}$ 26}	32.2	-196°C
{1 $\bar{1}$ 23}	16.4	-196°C

Table 2. Fracture surface energies of sapphire

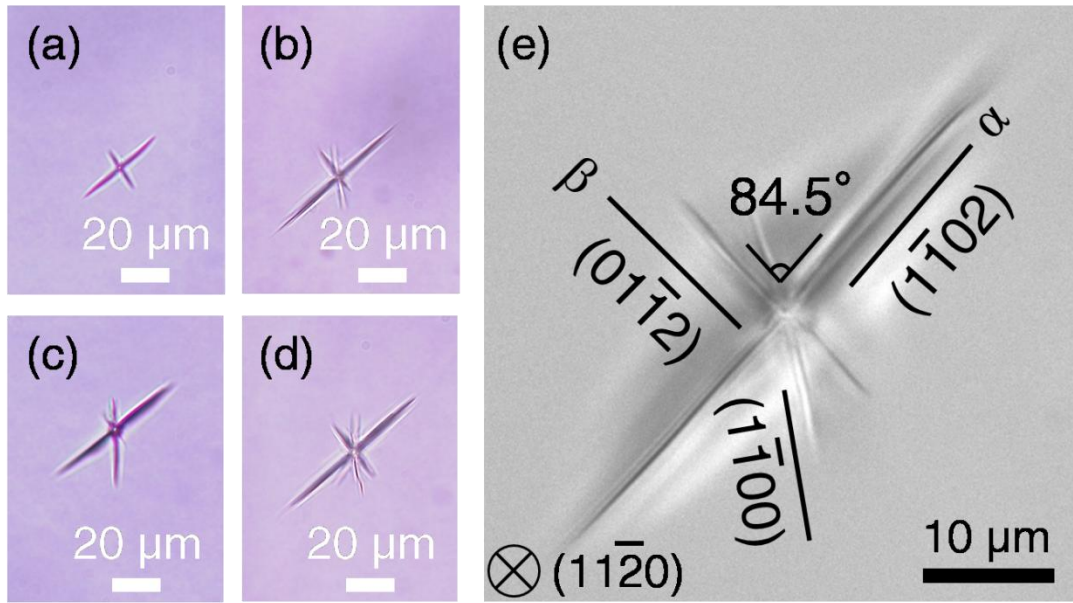


Figure 2.3 Top-view optical microscope photograph of the photomodified area in the $(11\bar{2}0)$ ruby sample irradiated with focused femtosecond laser beam with respect to the pulse energies of (a) 5, (b) 10, (c) 15, and (d) 20 μJ . (e) Crystallographic structures of the crack pattern. The cracks α and β were crossed at an angle of 84.5°

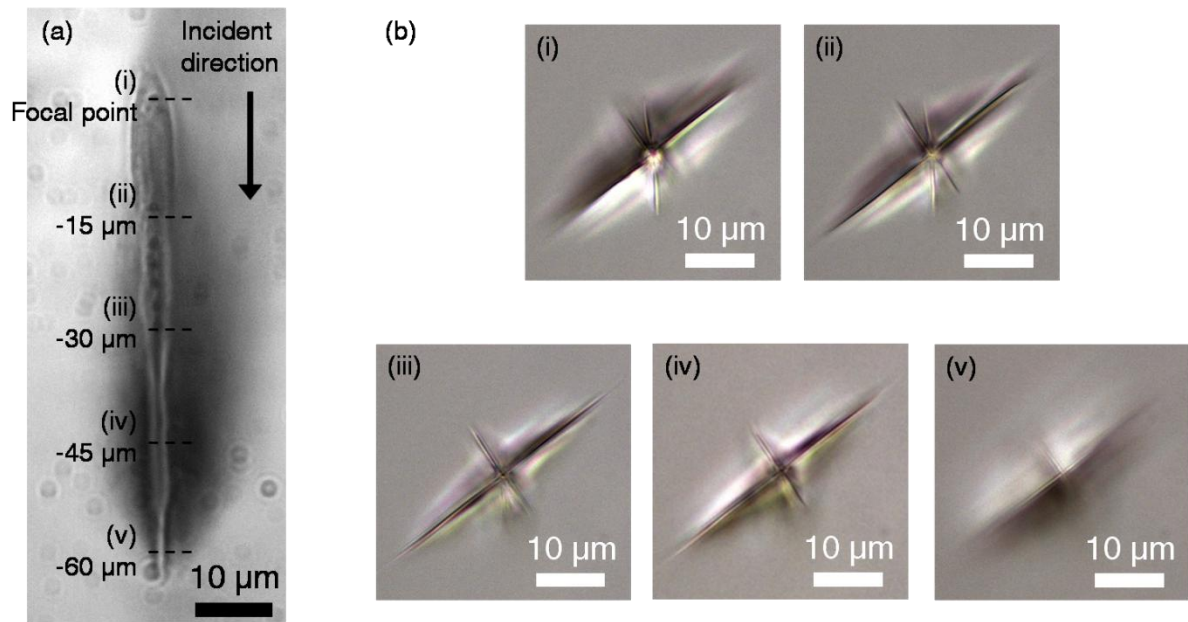
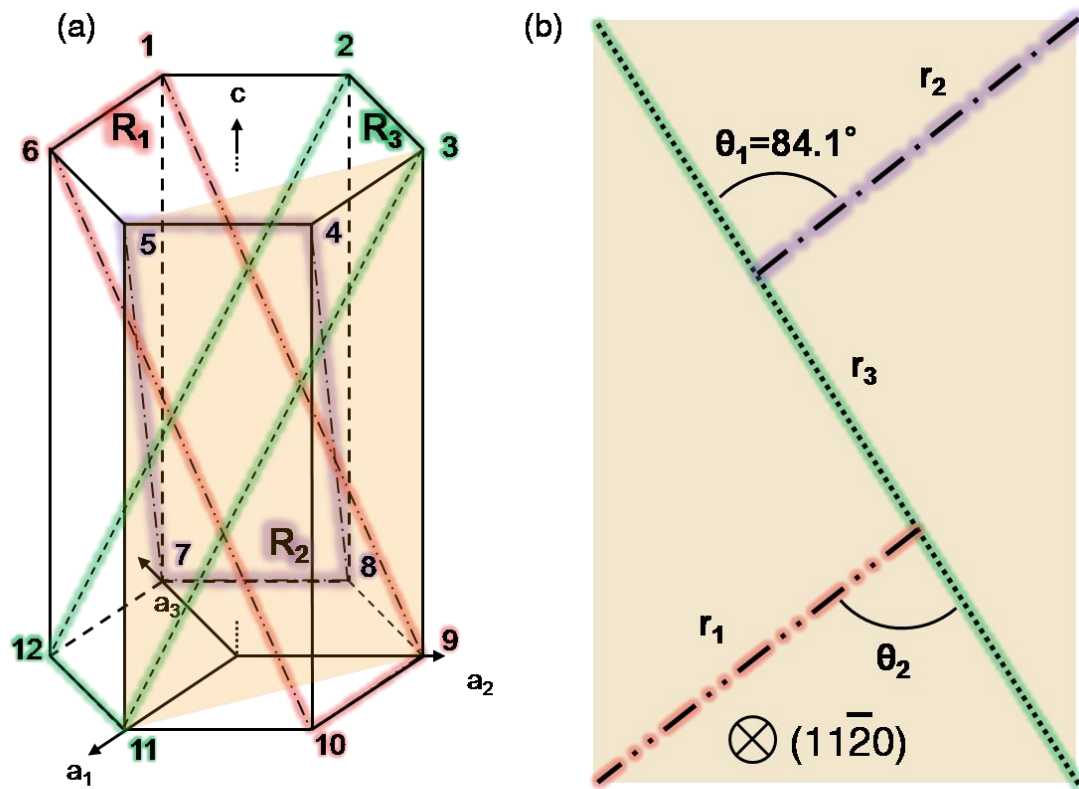


Figure 2.4 (a) Side-view optical microscope photograph of the irradiation site. (b) crack structures with respect to the depth from the focal point. Each depths were denoted in Fig. 1.4(a).

point to 15 μm , but they became invisible at more than 30 μm depth. The difference in depth of crack formations is also attributable to the fracture surface energy of each plane. Because the largest energy of laser was deposited at the focal point, both of the cracks on $\{1\bar{1}02\}$ planes and $\{\bar{1}100\}$ planes were formed near the focal point. On the other hand, the energy of laser became weaker as laser propagated, the cracks were formed only on $\{1\bar{1}02\}$ planes which had the lowest fracture surface energy than the other low-index crystallographic planes. The energy of laser deposited on the focal point will be discussed later.

We analyzed the morphology of the cracks on the basis of the crystal structure of sapphire. Figure 2.5 (a) shows a schematic illustration indicating crystallographic orientation of the corundum structure. R_1 , R_2 , and R_3 indicate the $\{1\bar{1}02\}$ rhombohedral planes, and the shaded plane is $(11\bar{2}0)$ plane. Each line r_1 , r_2 , and r_3 in Fig. 2.5 (b) corresponds to the intersected lines between each $\{1\bar{1}02\}$ planes and the $(11\bar{2}0)$ plane. Numerical calculation revealed that the angle θ_1 formed by r_2 and r_3 was 84.1° . The intersection lines r_1 and r_2 are parallel to each other, and therefore, angles θ_1 and θ_2 are equal. As compared to Fig. 2.3, the cracks on $\{1\bar{1}02\}$ planes corresponds to a combination of r_1 and r_2 , and the cracks on $\{\bar{1}100\}$ planes reflects r_3 , and the calculated angle θ_1 is in fairly good agreement with the measured one shown in Fig. 2.3. Therefore, it is confirmed that the cracks are mainly formed along the $\{1\bar{1}02\}$ rhombohedral planes and the $(1\bar{1}00)$ plane when the laser pulses were focused. Our results demonstrate that the unique crack patterns formed within ruby directly reflect the crystallography of the corundum structure.



R₁ plane : 1-9-10-6

R₂ plane : 4-5-7-8

R₃ plane : 2-3-11-12

Figure 2.5 (a) Schematic illustration showing crystallographic orientation of the corundum structure. Four planes are shown: R₁ (1-9-10-6); R₂ (5-7-8-4); R₃ (2-3-11-12); and shaded (5-3-9-11), which is the incident (11 $\bar{2}$ 0) plane. (b) Three intersection lines between the (11 $\bar{2}$ 0) plane and three rhombohedral planes. The calculated angle θ_1 between lines r_2 and r_3 was 84.1°, which coincided well with the experimental result.

Figure 2.6(a) shows a top-view optical microscope photograph of the photomodified area in the (0001) ruby sample irradiated with focused femtosecond laser beam with respect to the pulse energies of 10 μJ . The cracks formed by laser irradiation had asterisk-like structures and they were crossed at the angle of approximately 59.1° to each other. Figure 2.6(b) shows a schematic illustration of the intersection lines between (0001) plane and three R planes, which was analyzed from the crystallographic orientation of the corundum structure. The angles between three intersection lines were calculated to 60° . The cracks were formed along the rhombohedral planes on (0001) plane as well.

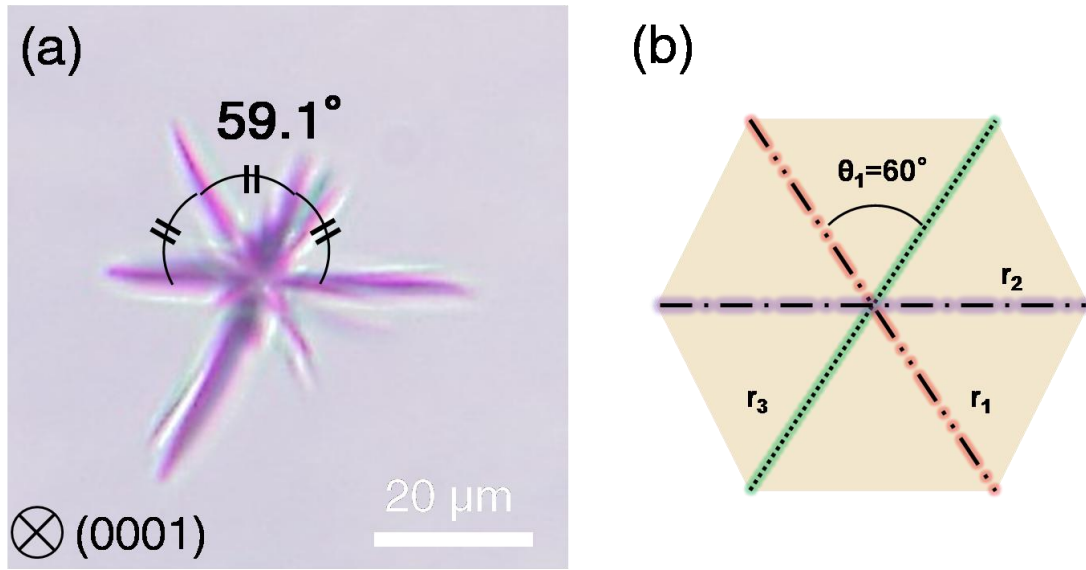


Figure 2.6 (a) a top-view optical microscope photograph of the photomodified area in the (0001) ruby sample (b) a schematic illustration of the intersection lines between (0001) plane and three R planes

2.3. The analysis of defect area by KOH etching

2.3.1. Experimentals

We used commercially available (11 $\bar{2}$ 0) sapphire with dimensions of 5 × 5 × 1 mm³ as a sample for laser irradiation. We were able to observe the top view of crack structure by polishing the surface of sapphire because the photomodified area had elongated to the incident direction of laser pulses. However, in the case of side-view observation, it was difficult to emerge the photomodified area having a diameter of less than 5 μm to the surface. Therefore, the laser irradiations were performed in two different ways: First, the conditions of laser irradiation mentioned in chapter 1.2 were adopted for the top-view observation. After the laser irradiation, we polished the sample approximately 60 to expose the focal point out of surface with diamond lapping films. Second, the sample was moved parallel to x-axis at a scan speed of 300 μm / s during the irradiation leaving behind line patterns. The sample was cut off perpendicular to the line patterns and the side surface was mechanically polished with diamond lapping films. The samples were etched by fused KOH for the range from 5 to 20 min at 280°C. The information of the surface structures before and after the etching was obtained by field-emission scanning electron microscope (FESEM, JEOL 6700F).

2.3.2. Results and Discussions

Figure 2.8 shows the SEM image of the photomodified area after KOH etching for 20 min. The center area consisting of the amorphous phase and polycrystals was heavily etched to the z-direction leaving behind a deep hole in the middle. The crack area on $(1\bar{1}02)$ planes was also etched to the z-direction and the crevices were formed indicating that the cracks had elongated shape along the direction of incident laser. On the other hand, the crack area on $(1\bar{1}00)$ planes was etched only near the surface, and the crevices on $(1\bar{1}00)$ planes due to the etching were shallow as compared with those on $(1\bar{1}02)$ planes. These results supported the optical microscope observations that the depths of cracks on $(1\bar{1}02)$ and $(1\bar{1}00)$ planes were different as shown in Fig. 2.3.

Figure 2.9(a) show a side view of the backscattered electron (BSE) image at the photomodified area and the corresponding optical microscope photograph was inserted in the same image. Figure 2.9 (b) and (c) show magnified BSE and SEM images of the area denoted 'a' in Fig. 1.11(a), respectively. The dark contrast was observed in BSE image which was aligned at intervals along the direction of incident laser. The dark area had hundreds of nanometers and the boundary of that area was vague. In SEM image, however, the surface of the dark area had no apparent differences with the surrounding. The surface information at the dark area excluded the possibility that the black dots would be voids. In addition, a BSE image reflects the information not only about a composition of the specimen but also about the lattice distortion if the specimen is a single crystal. Therefore, we estimated that the dark contrast area contained highly dense dislocations which were formed at outer edge of the focal point as shown in Fig. 1.2(a).

We conducted the etching of the sample after the laser irradiation to confirm the existence of dislocation, because if a crystal containing dislocations is subjected to an etching, the rate of etching around the dislocations may arise due to the lattice distortion and strain field of the dislocation. Figure 2.10 shows a side view of SEM image after KOH etching for (a) 5, (b) 10, (c) 15, and (d) 20 min. After 5 min of etching, the dot areas were preferentially etched so that the discrete depressions were formed having corresponding morphology to the dark contrast as shown in Fig. 1.11(a). The photomodified area was entirely etched after 20 min. The preferential etching at the dark contrast area revealed that the density of dislocations at that area was higher than at the surroundings, and entire etching of the photomodified area was attributed to the amorphous Al_2O_3 phase which had a higher reactivity to acidic solutions.¹³ Figure 2.11 shows a schematic illustration of the photomodified area after laser irradiation.

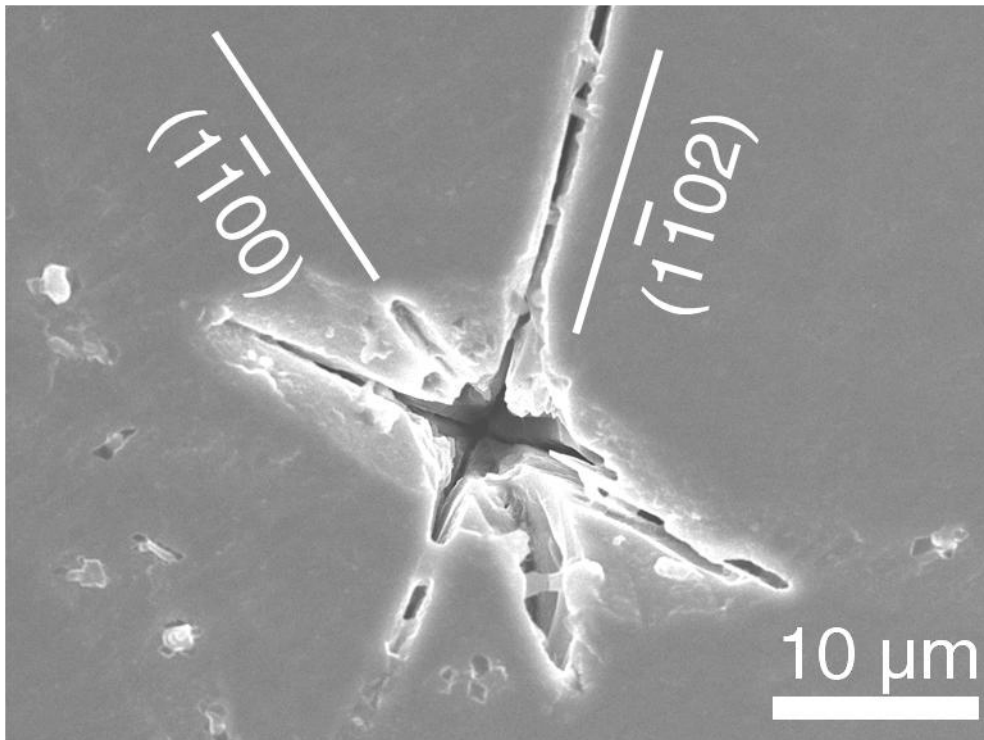


Figure 2.8 FESEM image at the photomodified area after KOH etching.

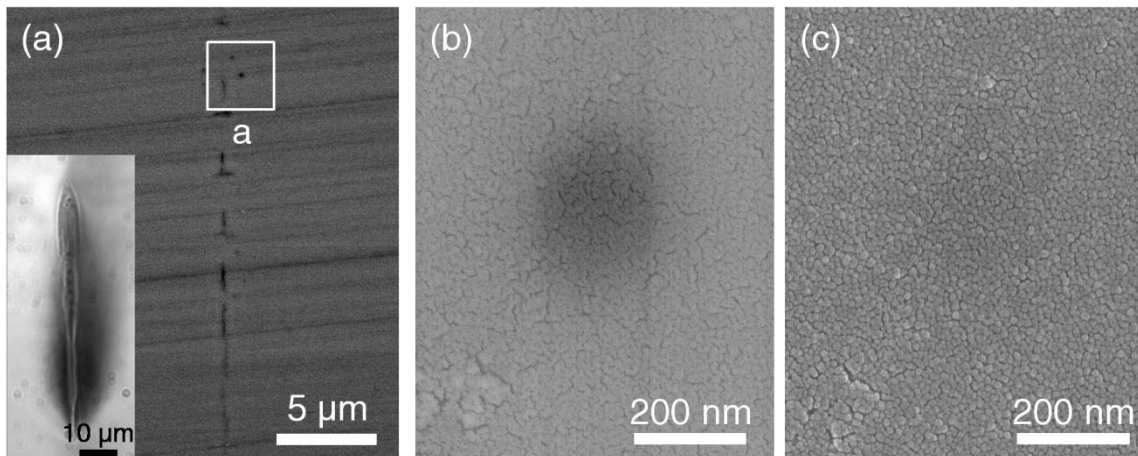


Figure 2.9 (a) a side view of the backscattered electron (BSE) image at the photomodified area and the corresponding optical microscope photograph (inset). (b) Magnified BSE image and (c) magnified SEM image of the single dot denoted 'a' in Fig. 1.11(a)

Figure 2.12 (a) shows a crossed Nicols bright-field image of the ruby sample at the photomodified area. The bright area indicates the existence of the residual strains around the focal point after laser irradiation. It shows that the residual strains at the photomodified area were distributed perpendicular to the cracks. The asymmetric distribution of the residual strains is ascribed to the difference of fracture surface energies of sapphire. While the energy of laser pulses exerted on sapphire propagated radially from the focal point, it was used as an activation energy for the crack formations on the $\{1\bar{1}02\}$ and $\{1\bar{1}00\}$ planes having low fracture surface energies as shown in Fig. 2.1. As a consequence, the energy of the laser pulses in other areas produced the residual strains within the crystal lattice with an asymmetric distribution normal to the direction of the cracks.

Figure 2.12 (b) shows a mapping image of the peak shift of the ruby fluorescence around the crack. The red and blue shifts indicate compressive (yellow dots around α and β) and tensile stress (black dots around δ and γ), respectively. The peak shifted toward longer and short wavelength approximately 0.04 nm at the center and the crack tip area, respectively. The maximum residual stresses were calculated to be 0.11 GPa for both the compressive and the tensile stress.¹² The distribution of red shift corresponded with that of bright area shown in Fig. 2.6 (a), indicating that the residual strain at α and β had compressive component.

Figure 2.13 shows the change in the average length l as a function of the number of laser pulses at various pulse energies. An optical microscope photo of the ruby sample after laser irradiation at a pulse energy of 5 μ J is shown (inset). As the number of pulses increased, the length l increased drastically below 500 laser pulses; however, it exhibited a moderate increase over the next 500 pulses. Also, the lengths of the crack increased with increasing pulse energy.

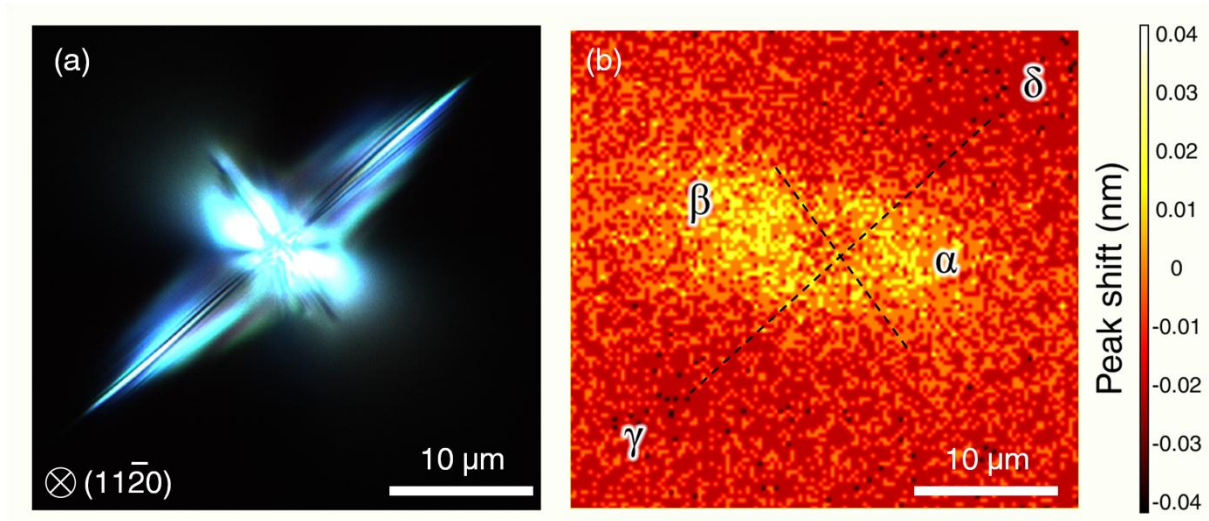


Figure 2.12 (a) Crossed Nicols bright-field image (10 μJ , 4000 pulses). (b) Peak shift mapping of ruby fluorescence R1 line in the vicinity of the focal point. The dashed lines represent the traces of nanocracks. The yellow dots representing red shift were attributed to compressive stresses and were distributed along the nanocracks. The black dots representing blue shift were attributed to tensile stresses, and were notably found at γ and δ corresponding to the ends of a nanocrack.

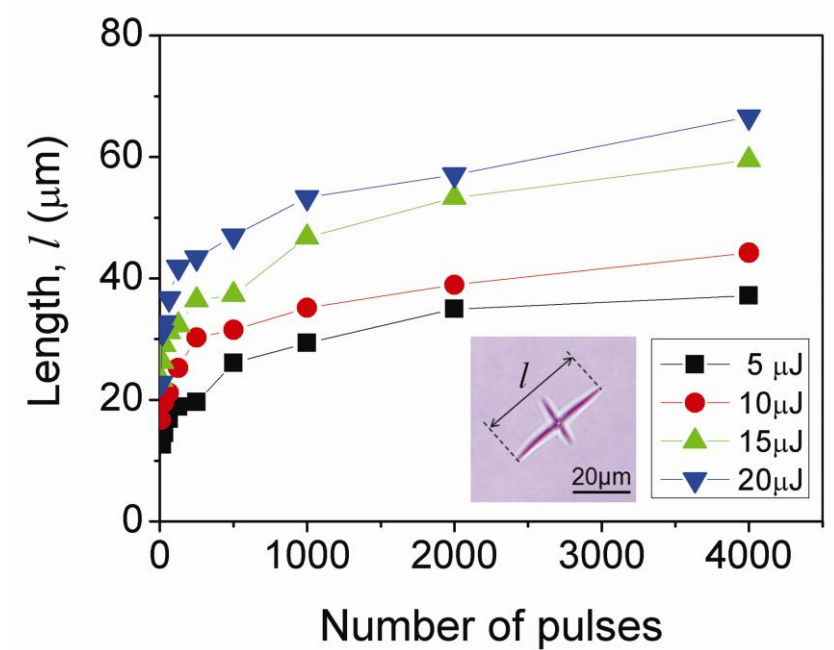


Figure 2.13 Plot of average length l of the crack along line (1) as a function of the number of pulses.

Therefore, the length of a nanocrack presumably depends on the magnitude of stress under given laser irradiation conditions.

2.4. Conclusions

In this chapter, we have investigated the deformation mechanism of ruby in a microscopic area by focused femtosecond laser irradiation. There were three distinct changes after laser irradiation. First, phase transformation from single crystalline to amorphous phase occurred at the center of the focal point. Second, dislocations were formed at the surrounding of the amorphous phase, and the density of the dislocations was quasi-periodically fluctuated with the depth from the focal point. Third, nanocracks having a width of approximately 30 nm formed along the $\{1\bar{1}02\}$ rhombohedral planes and the $\{1\bar{1}00\}$ plane regardless of the orientation of the incident laser and the size of the cracks depended on the irradiation condition of the laser. The results of this chapter can be applied to the radiation-free crystal orientation analysis of sapphire by investigating the direction of crack propagation after femtosecond laser irradiation.

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Chapter 3

Changes of Defect Morphology after Heat Treatments subsequent to Femtosecond Laser Irradiation

3.1. Introduction

The defects in a single crystal such as dislocations, pores, and cracks have been extensively studied since it affects to the mechanical and electrical properties of the crystal. In particular, sapphire ($\alpha\text{-Al}_2\text{O}_3$) is one of the most important ceramic materials and its applications such as a substrate for semiconductor devices and a solid-state laser medium are extremely sensitive to defects. Attempts have been made for decades to control the defects of sapphire, and among of them, an annealing is well-established technique to decrease and eliminate defects of sapphire. The defects of sapphire can shrink by heat treatments, and particularly, a diffusive healing process occurred around crack is called “crack healing”¹. For a cylindrical crack, the morphological changes of cracks by the annealing depend on the aspect ratio (length to diameter, L/D) of the initial crack via Rayleigh instability²; cracks would be split into a string of spheres when $L > 2\pi D$ or convert directly to a sphere when $L < 2\pi D$ ³.

Many useful methods have been used to investigate the behaviors of the crack healing in sapphire. The most commonly used methods for introducing cracks into sapphire include indentation, impact, and abrasion, however formations of cracks by these methods were restricted only on the surface of sapphire specimens⁴⁻⁶. On the other hand, ion beam etching in combination with bonding method allows embedment of cracks at the internal interface of sapphire bicrystal^{7; 8}. However, this technique requires a complex procedure for a sample

preparation and sizes of such cracks are typically in the micrometer range, and most of all, the embedded cracks are initially formed on the surface of sapphire rather than inside sapphire from the beginning. Because of these instrumental limitations, few reports exist about the healing behaviors of cracks which are formed truly inside sapphire.

Recently, femtosecond lasers have attracted considerable attention because they can focus a large amount of energy on a microscopic area inside various transparent materials without surface damage.⁹⁻¹¹ In addition, the structural changes with a nanometer size often occur after the laser irradiation, which is smaller than the laser wavelength.¹²⁻¹⁴ We previously reported that cracks having a width of approximately 30 nm were formed inside sapphire via femtosecond laser irradiation,(ref) and their direction and length depended on the crystal orientation and laser irradiation conditions.

Here, we report the thermally activated morphological evolution of nanometer-scale cracks formed inside sapphire. We used femtosecond laser to introduce cracks inside sapphire, and performed high-temperature heat treatment above 1200 °C that resulting in the crack healing process. The amorphous phase formed at the focal point after the laser irradiation returned to the crystalline phase by the annealing, leaving behind dislocation structures. The cracks formed along the $(1\bar{1}02)$ and the $(1\bar{1}00)$ planes transformed into the channel of periodic pores by the annealing. Evaluating the Raman shift around the focal point after laser irradiation and subsequent heat treatment, we discuss the crack healing process in terms of a relaxation of residual strain and a recovery of crystallinity.

3.2. Experimental

We used (11 $\bar{2}$ 0) sapphire with dimensions of $10 \times 10 \times 1 \text{ mm}^3$ as a sample. A femtosecond laser having a pulse width, wavelength, and repetition rate of 238 fs, 780 nm, and 1 kHz, respectively, was used as the optical source (IFRIT, Cyber laser). The pulse energy and number of pulses at the sample location were controlled by a neutral density (ND) filter and fast electronic shutter, respectively. A laser beam with a diameter of 5 mm in Gaussian mode was focused at a depth of 50 μm from the sample surface using a microscope objective lens (Nikon, 100x) with a numerical aperture (NA) of 0.9. The incident laser beam was normal to the (11 $\bar{2}$ 0) plane of the sample. The heat treatment was carried out in the range from 1200 to 1500 °C in air to investigate the thermally activated change of the crack morphology. The holding time at the annealing temperatures was changed between 1 and 20 hours. The structural changes around the focal point after laser irradiation and subsequent heat treatment were observed using optical microscope and transmission electron microscope (TEM, JEOL 2010HC, 200kV). TEM sample was prepared by a standard procedure using ion thinning method. The peak shift and the full widths at half maximum (FWHM) of the Raman spectra at the photomodified area were measured at room temperature by confocal Raman spectroscopy (Nanofinder® 30, Tokyo Instruments) to analyze the residual strain and the crystalline quality around the focal point. Frequency-doubled Nd:YAG laser operating at 532 nm was used for Raman excitation. Raman spectra were calibrated with respect to the wavelength of the excitation light, and they were recorded using an air-cooled CCD detector having a resolution of 1.64 cm^{-1} and operating at $-60 \text{ }^\circ\text{C}$. The spatial and spectral resolution of the Raman microscope (100x objective, NA = 0.9) was approximately 275 nm and 0.98 nm, respectively.

3.3. Results and Discussions

Figure 3.1(a) shows a bright-field TEM image and an optical microscope image (upper left) of the photomodified area in the sapphire sample after the laser irradiation. The sample was irradiated with 1000 laser pulses with a pulse energy of 3 μJ . The center area of the focal point having a diameter of approximately 2 μm was extremely deformed by laser irradiation. The deformed area comprised the mixture of amorphous and polycrystalline phase in the middle, and dislocations in the edge.^{15; 16}(ref Moon) In addition, cracks were formed around the focal point. The cracks having a width of approximately 30 nm were parallel to the $\{1\bar{1}02\}$ and $\{1\bar{1}00\}$ planes which had a minimum surface fracture energy¹⁷. We estimated that the cracks on $\{1\bar{1}02\}$ planes existed at different depths, because the crack on $(01\bar{1}2)$ plane (dashed line) was not observed in TEM image due to the thinning procedure.

Figure 3.1(b) shows a bright-field TEM image and an optical microscope image (upper left) of the photomodified area after the heat treatment at 1500 $^{\circ}\text{C}$ for 10h. The amorphous phase at the focal point was completely transformed back into a crystalline phase by the heat treatment, owing to the stability of Al_2O_3 crystalline phase at higher than 1300 $^{\circ}\text{C}$.¹⁸ Additionally, the channel of spherical pores was aligned along the path of cracks. It is suggested that the crack healing occurred by heat treatment, so that the cracks evolved into arrays of discrete pores. Also notable is the fact that the dislocations, linear defects in crystals around which arrays of atoms were irregular, were formed. The dislocations had a network structure at the very center of the focal point, in contrast, they were distributed quasi-periodically along the $(1\bar{1}02)$ plane. We estimated that the network structure of the

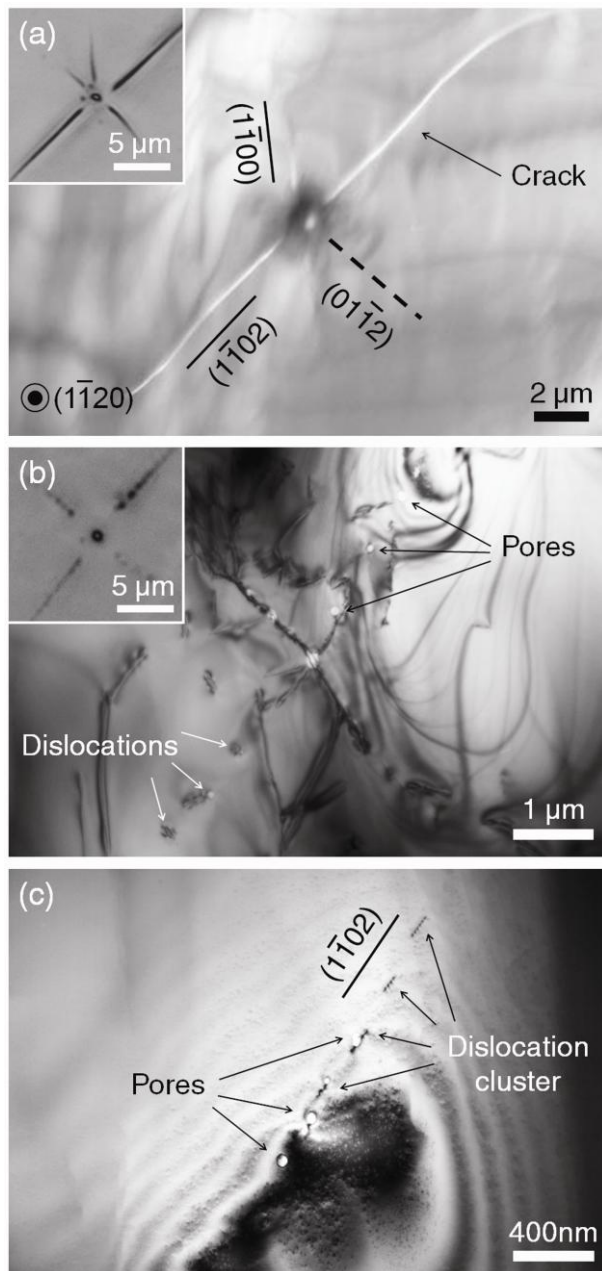


Figure. 3.1 (a) a TEM image at the focal point after femtosecond laser irradiation with 1000 laser pulses of 3 μJ pulse energy, (b) a TEM image at the focal point after the annealing, (c) a TEM image at the crack tip area after the annealing.

dislocations originated from the recrystallization over a range of the amorphous phase, while the formation of the quasi-periodic structure was attributable to the crack healing.

Figure 3.1(c) shows a bright-field TEM image of the crack tip area. Array of quasi-periodic pores was also observed along the $(1\bar{1}02)$ plane, however, the value of R and λ of the pores at the crack tip area was 26 nm and 230nm, respectively, which was smaller than that at the center area as shown in Fig. 3.1(a). In crack healing, the formation of discrete spherical pores depends upon the aspect ratio of a crack via Rayleigh instabilities, therefore, the distances between isolated pores, λ , are a function of the crack width.^{7; 19-21} Because the value of λ decreased with increasing distance from the focal point as shown in Fig. 1, we could estimate that the further the cracks propagated from the focal point, the narrower the crack widths became.

In addition, dislocation clusters consisting of more than one dislocation were formed along the $(1\bar{1}02)$ plane and they were almost constantly separated at intervals of approximately 300 nm as shown in Fig. 3.1(c). These periodic structures of dislocation clusters were also found at the grain boundary of sapphire bicrystal with a low-angle tilt grain. In the case of sapphire bicrystal, groups of dislocations separated by almost constant separation distances of about 230 nm were introduced to compensate tilt and twist components of the low-angle boundary which were induced during the formation of the bicrystal.²² The formation of periodic dislocation clusters in our work can be understood in the same way; when the cracks closed via diffusive crack healing process by the annealing, the opposing interfaces of the cracks are connected and they stick together which lead to the formation of a grain boundary. Because the opposing interfaces of the cracks do not completely match each other and have misorientations at the grain boundary, small amount of tilt and twist is introduced into the grain boundary. Consequently, dislocation clusters should be introduced to relieve the strain

at the grain boundary, which resulted in the alignment of dislocation clusters along the trace of the cracks.

Figure 3.2(a) shows optical microscope images of discrete pore channels at different depths of (i) 0, (ii) 10, and (iii) 20 μm from the focal point after the heat treatment, and the depths of the observation were shown in Fig.3.2(iv). The locations of the pore channels at different depths were illustrated in Fig.2(a)(v). The channels of the discrete pores formed along the $(1\bar{1}02)$ plane regardless of the depths, however they did not overlap completely each other. It means that the cracks had the shape of an independent cylinder rather than a planar shape, and the transformation from the crack into the discrete pores occurred within the specific cylindrical crack by heat treatment. Figure 3.2(b) shows the relationship between the normalized pore spacing (λ/D) and the annealing time at 1500 $^{\circ}\text{C}$, where λ is distance between neighborhood pores for these channels and D is a diameter of a pore. The value of λ/D was nearly 1 after the 1 hours of annealing. At this time, the healing process had just started so that the narrowing and the bulge of the crack began to occur, however the crack having unduloid-like shape did not break into multiple spheres yet. The value of λ/D became larger with the increase of the annealing time, implying that the crack split into the discrete pores, and the diameter of the pore decreased as the crack healing proceeded further. The schematic illustration of the crack healing process was shown in Fig.3.2(c). Because the length L of the crack was larger than the width D of that, i.e. $L \gg 2\pi D$, the crack would alter its form by surface diffusion after heat treatment, according to the Nichols–Mullins hypothesis²³; it narrows at one point and bulges at another. As the evolution of the crack proceeds, the crack having unduloid-like shape reduces its surface energy by transforming into a channel of isolated spheres via Rayleigh’s instability^{1, 24}.

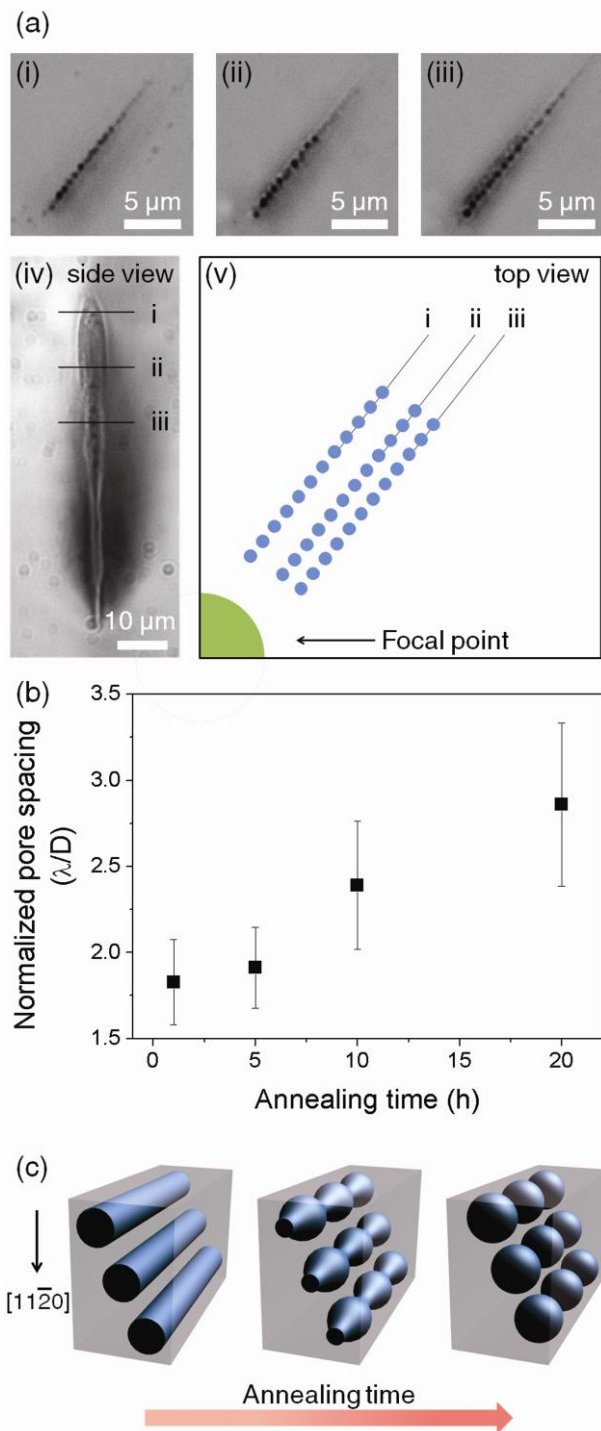


Figure. 3.2 (a) Bright-field TEM image of sapphire around the focal point after the annealing subsequent to laser irradiation, (b) Bright-field TEM image of sapphire around the crack tip area.

Consequently, individual cracks became the channels of discrete pores having different depths.

Figure 3.3 shows crossed Nicols bright-field images of sapphire (a) after the laser irradiation and (b) after the subsequent annealing at 1300 °C for 5 hours. The bright area in Fig. 3.3(a) indicates the existence of the residual strain around the focal point after the laser irradiation. The asymmetric distribution of the residual strain is ascribed to the difference of fracture surface energies of sapphire: while the energy of laser pulses exerted on sapphire propagated radially from the focal point, it was used as an activation energy for the crack formations on the $\{1\bar{1}02\}$ and $\{1\bar{1}00\}$ planes having low fracture surface energies as shown in Fig. 3.1. As a consequence, the energy of the laser pulses in other areas produced the residual strain within the crystal lattice with an asymmetric distribution. After the annealing, however, the bright area almost disappeared as shown in Fig. 3.3(b), which manifested relaxations of the residual strain around the focal point.

To investigate the relationship between the crack healing process and a relaxation of residual strain at the photomodified area, we examined the effect of the heat treatment on Raman spectra at the focal point. Figure 3.3(c) shows Raman spectra at the photomodified area of sapphire before and after annealing subsequent to laser irradiation. The Raman spectrum of as-received sapphire was also shown in the same figure as a reference. The Raman peaks of sapphire were detected at 378, 417, 645 cm^{-1} regardless of laser irradiation and the annealing, though, we adopted a wavenumber of 417 cm^{-1} as a criteria originating from Raman allowed A_{1g} vibration of sapphire, because it was the strongest peak among the Raman active phonon modes of $(11\bar{2}0)$ sapphire.²⁵ Table 1 shows the center peak wavenumber and the corresponding full widths at half maximum (FWHM), already known as an indicator of the crystalline quality²⁶, of Raman spectra in sapphire we have

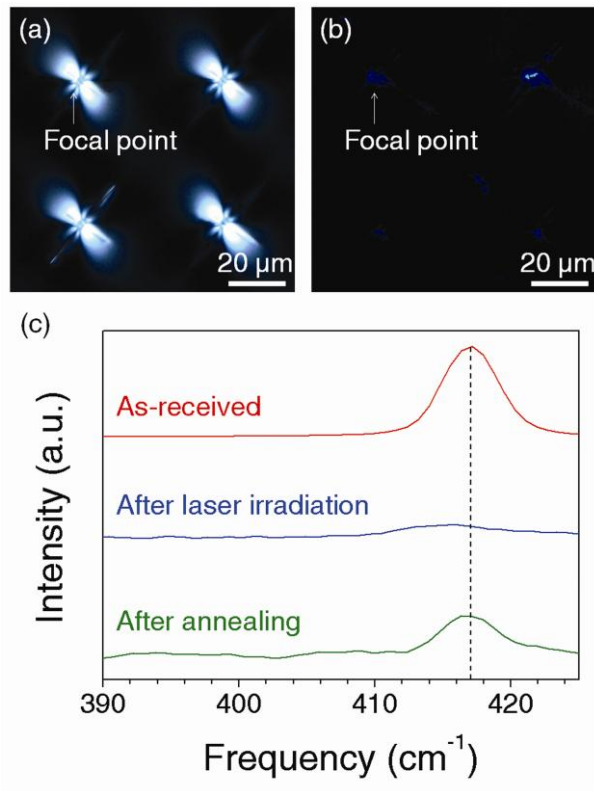


Figure. 3.3 (a) Crossed Nicols bright-field image of the photomodified area after laser irradiation, (b) after the annealing subsequent to laser irradiation. Two images were obtained with the same exposure time. (c) Raman spectra obtained from as-received sapphire, the photomodified area of sapphire after laser irradiation, and after the subsequent annealing. The vertical dashed line at 417 cm^{-1} represents a reference Raman frequency of as-received sapphire.

investigated. The values of FWHM were calculated with respect to a baseline obtained by drawing a tangent line to the spectrum between 300 and 800 cm^{-1} . Raman peak at 417 cm^{-1} shifted to 415.3 cm^{-1} after the laser irradiation due to the tensile residual strain, however, it showed a blue shift to 416.3 cm^{-1} after the annealing. Therefore, it is confirmed that the residual strain at the photomodified area were predominantly relaxed to lower the total surface energy of the cracks by the annealing which was in accordance with our polarizing microscope observation. In addition, the FWHM increased from 3.6 cm^{-1} to 11.2 cm^{-1} after laser irradiation, indicating that the crystalline quality at the photomodified area degraded by the laser irradiation²⁷. However, the FWHM of the annealed sample recovered the value close to that of as-received sapphire. We estimate that the increase of the FWHM is due to the amorphization and the crack formations around the focal point by the laser irradiation, and the recovery of the FWHM is due to the recrystallization and the crack healing via the heat treatment. However, the dislocations as shown in Fig. 3.1(b) resulted in the incomplete recovery of the FWHM even after the annealing.

Figure 3.4(a) shows the optical microscope images after annealing at 1500 °C with different annealing times. It can be seen that the phase transformation from an amorphous to a crystalline and the crack healing proceeded as the annealing time increased. Figure 3.4(b) shows the heat treatment conditions in which the formation of discrete pore channels was confirmed by optical microscope observations. We noticed that crack healing effect depended on the annealing temperature: that is, the crack healing was observed only after annealing above 1300 °C for more than 5 hours. Accordingly, it is estimated that 1300 °C is the critical annealing temperature which can activate the diffusive crack healing process. It is worth pointing out that this critical temperature for crack healing corresponds to a brittle-to-ductile transition temperature of sapphire^{5; 28} above which the dislocation activity increases. The

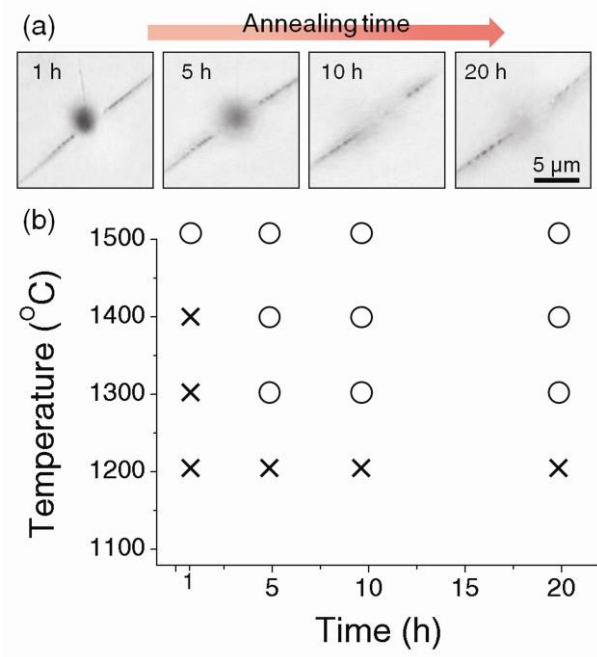


Figure. 3.4 the optical microscope images at the focal point after the different annealing temperature of (a) 1200 (b) 1300 (c) 1400 and (d) 1500 °C. (e) the annealing conditions in temperature and time. ○ indicates the condition in which crack healing was observed, and × not observed.

enhancement of atom mobility above 1300 °C is considered as one of the causes of diffusive healing process.

	Peak position (cm ⁻¹)	FWHM (cm ⁻¹)
As-received	417.1	3.6
After laser irradiation	415.3	11.2
After annealing	416.3	5.5

Table 3.1 the center peak wavenumber and the corresponding full widths at half maximum (FWHM) of Raman spectra in sapphire

3.4. Conclusions

In summary, we presented a simple one-step process for introducing nanometer-scale crack inside sapphire and investigated the morphological changes of the internal cracks through the thermal activation. We found that the cracks formed inside sapphire by femtosecond laser irradiation evolved into the channel of discrete pores by the subsequent heat treatment above 1300 °C, and the pore channels were aligned along the specific crystal orientation. Raman survey at the focal point revealed that the driving force of the transformation was the decrease in the surface energy through the relaxation of residual strain. The method we have shown here can help in studying behaviors of intrinsic defects inside various transparent materials without disturbance of external factors. Besides, because this technique can induce the directionally-aligned dislocations inside sapphire, it can be also applied to the formation of a shape-controlled dislocation structure which can exhibit unusual physical properties such as conductivity in insulating ceramics.

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Chapter 4

Long-lasting phosphorescence of oxygen Defects in perovskite type oxide

4.1. Introductions

Long-lasting phosphorescence (LLP) is the light emission that persists for a long time after stopping irradiation of excitation light such as sunlight or artificial UV light. Long-lasting phosphors have attracted considerable attention in the recent half-century and can be widely used in areas such as safety indication, lighting in emergency situation, luminous paint, and so on. This delayed light emission arises from the fact that charge carriers (i.e., electrons and/or holes) generated by the excitation are trapped at certain defect sites, and their detrapping is thermally activated. Besides luminescent centers, the phosphorescence phenomenon requires the presence of certain discrete levels within the forbidden band gap, which are associated with chemical and/or physical defects of the host lattice (e.g., dopants and vacancies). Under UV irradiation, some electrons and/or holes generated by the excitation are trapped in such localized levels. Due to a spatial separation between these defects and the luminescent centers (or more precisely, due to the lack of their orbital overlap), the probability of direct recombination is very low. Consequently, trapped charge carriers are maintained in a metastable state (i.e., the excitation energy is stored), as long as there is no energy supply for detrapping them and hence inducing their recombination. Currently, most of efficient long-lasting phosphors are composed of alkaline-earth aluminates doped with rare-earth ions. Such dopants act as an electron trap lying between the valence and conduction band of the materials.

Here, we report new long-lasting phosphor, BaZrO₃:Ti perovskite. In this study, oxygen vacancy, one of the most common defects inside oxides, combined with cation provided an electron trap instead of rare-earth ions. Oxygen vacancies represent one of the most common point defects in oxides. Depending on the nature of the material, ionic, covalent, or mixed, the removal of an O atom from the lattice or from the surface results in a different electronic and geometric rearrangement of the structure. In ionic oxides, the removal of a neutral O atom from a lattice results in a cavity and two electrons. The two electrons are confined in the cavity region by the effect of the strong Madelung field, giving rise to an *F* center, a point defect with specific optical properties which is responsible for the coloring of the sample. Phosphorescence properties of BaZrO₃:Ti perovskite, especially the effect of additive TiO₂ on LLP were investigated, and the mechanism was also discussed.

4.2. Experimental

BaZrO₃:Ti was synthesized by a standard solid-state reaction. Stoichiometric mixtures of BaCO₃, ZrO₂ and TiO₂ (0 - 3 mol% for ZrO₂) were milled in a mortar and pressed into pellets, and then calcined at 1300°C for 6 hours in air. The crystal structure of the obtained sample was verified by X-ray powder diffraction (XRD). XRD pattern was measured using Cu K α radiation in the range $10^\circ < 2\theta < 80^\circ$ with an angle step of 0.02° (Rigaku RINT-2500HF diffractometer). Electron spin resonance (ESR) spectra of the sample in powder form were recorded at room temperature using an X-band spectrometer (JEOL JES-TE100) with a 100 kHz field modulation. Absorption spectra were measured using a spectrophotometer (JASCO V-570) equipped with an integrating sphere reflectance attachment (ISN-470). Photoluminescence spectra and phosphorescence decay curves were measured with a fluorescence spectrophotometer (Jobin-Yvon/Horiba Fluoromax-P). Phosphorescence decay curve was obtained by recoding the photoluminescence peak intensity with time, after removal of excitation light; excitation wavelength and irradiation time were 274 nm and 5 minutes, respectively. The obtained decay curve was analyzed using Origin 7.5J.

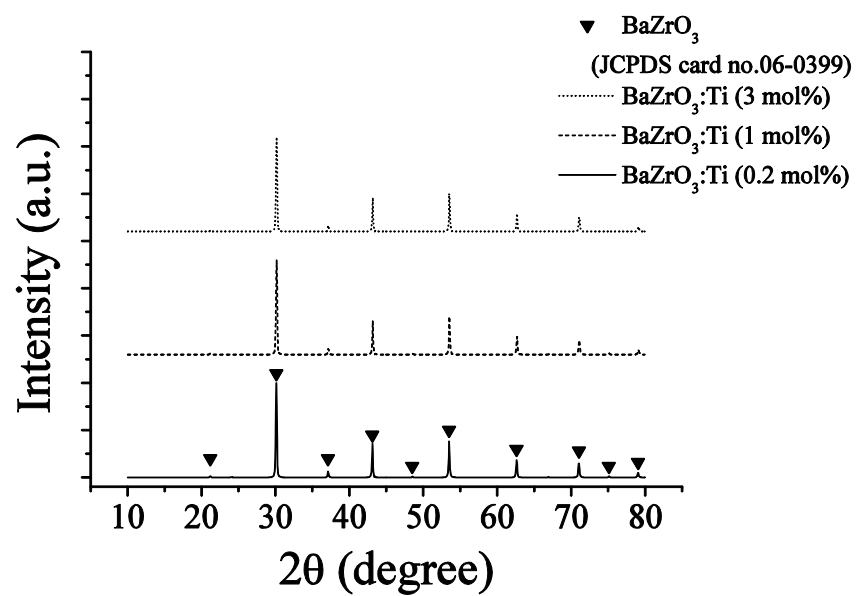


Figure 1. The XRD patterns of the prepared $\text{BaZrO}_3\text{:Ti}$.

4.3. Results and discussion

Figure 4.1 shows the XRD pattern of the prepared Ti-doped BaZrO₃. The patterns with the doping amount of 0.2 ~ 3 mol% showed no impurity peaks and were attributed to that of BaZrO₃ cubic perovskite with space group $Pm\bar{3}m$ (JCPDS card no. 06-0399), indicating that almost all of the additive Ti ions were successfully incorporated into the Zr ion site; in the ABO₃ perovskite structure, if the twelvefold coordination site (“A” site) is occupied by Ba ion, Ti ion will occupies the sixfold coordination site (“B” site) owing to the electroneutrality and the difference in ionic radii, as in BaTiO₃.

Figure 4.2 shows the photoluminescence excitation (PLE) spectrum, photoluminescence (PL) spectrum, and LLP spectrum of the 0.2 mol% Ti-doped BaZrO₃. The LLP spectrum was measured five minutes after blocking UV excitation light (wavelength: 274 nm, irradiation time: 30s). The PLE and PL spectra have peaks at 274 nm and 408 nm, respectively. It is noted that no luminescence was observed from undoped BaZrO₃ over excitation wavelengths: from 250 to 700 nm. Both PL and LLP spectra showed violet-blue broad-band emission and almost the same spectral shape, leading us to presume that PL and LLP arose from the same luminescence center. Figure 4.3 shows absorption spectra of the 0.2 mol% Ti-doped and undoped BaZrO₃. Additional absorption band was observed at around 270 nm, which is similar to PLE band for PL. It is also deduced that the interband optical absorption efficiency of BaZrO₃ is low for 270 nm excitation light.

Dependence of PL peak position and intensity on the additive amount of TiO₂ is shown in Fig. 4.4. From 0.05 mol% to 0.5 mol% TiO₂, PL spectra of BaZrO₃:Ti had a peak at around 408 nm and luminescence color was violet-blue. Additional doping shifted the PL peak position to longer wavelength region: 420 nm (in 0.8 mol% TiO₂) and 450 nm (3 mol%). Therefore, emission color changed from violet-blue to green over the range of 1 - 3 mol%

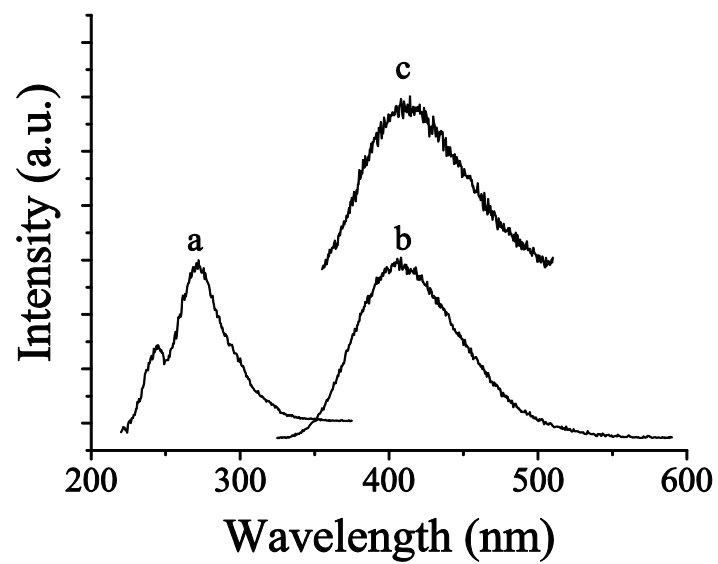


Figure 4.2. Optical spectra of BaZrO₃:Ti phosphor: (a) PLE spectrum (Em λ = 408 nm), (b) PL spectrum (Ex λ = 274 nm), and (c) LLP spectrum 5 min after stopping the UV light (λ = 274 nm).

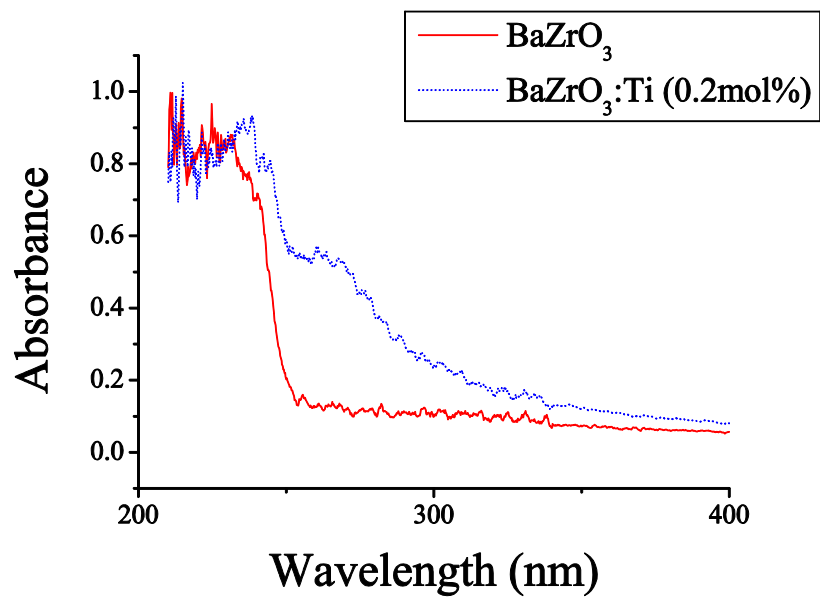


Figure 4.3. Absorption spectra of undoped and 0.2 mol% Ti-doped BaZrO_3 .

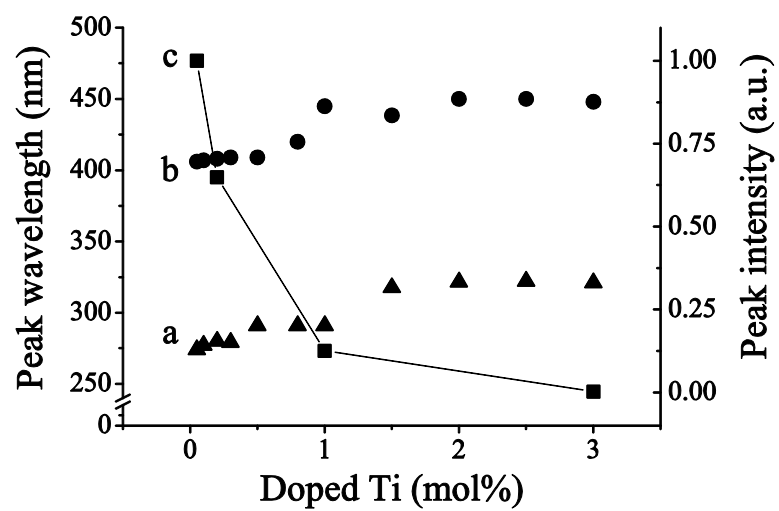


Figure 4.4. Plot of peak positions of PLE spectra, ▲, and peak positions of PL spectra, ●, and peak intensities of the PL spectra, ■, of the prepared BaZrO₃:Ti against the additive TiO₂ concentration.

TiO₂. On the other hand, PL intensity considerably decreased as the additive amount of TiO₂ increased.

Figure 4.5 presents the ESR spectra of the prepared BaZrO₃ doped with various amount of TiO₂. We can see the presence of three dominant ESR lines at $g = 2.004$, $g_{\perp} = 1.974$, $g_{\parallel} = 1.957$, even in non-luminescent undoped BaZrO₃. The signal of $g = 2.004$ can be assigned to F^+ centers, i.e., singly charged oxygen vacancies [6-8]. The other two signals, $g_{\perp} = 1.974$ and $g_{\parallel} = 1.957$, are attributable to Zr^{3+} [8-10]. Both the ESR signal intensities of F^+ center and Zr^{3+} decreased with increasing additive amount of TiO₂, implying that their concentrations decreased with increasing additive TiO₂. It is also deduced that luminescence center is neither F^+ center nor Zr^{3+} . However F^+ center and/or Zr^{3+} may play a role of trapping electron or hole derived from UV excitation; trapping and detrapping the light-induced electron and/or hole through defect center is an important process for LLP [3]. Since both PL and LLP were observed only from Ti-doped BaZrO₃, additive TiO₂ can produce a luminescence center. Considering the obtained ESR spectra and the electronegativity of Ti (1.3) larger than that of Zr (1.2), it is expected that additive TiO₂ induces the following reaction: $Zr^{3+} + Ti^{4+} \rightarrow Zr^{4+} + Ti^{3+}$. We expect F_A center to be the luminescence center in the Ti-doped BaZrO₃. F_A center is a complex of anion vacancy (partially or fully filled by electron) and cation [6, 11], and in this case, is the defect pair of F^+ center and Ti^{3+} . F_A center is known as a potential luminescence center [12-14]. Formation of F_A center can support the above reaction scheme, since the coupling of F^+ center and Ti^{3+} can explain both no observation of ESR signal of paramagnetic Ti^{3+} and decrease in ESR signal intensity of F^+ center by adding TiO₂. However, short spin-lattice relaxation time may be a reason for no detection of Ti^{3+} by room temperature ESR measurement. In any case, it is noted that Ti^{3+} itself cannot be a luminescence center of the

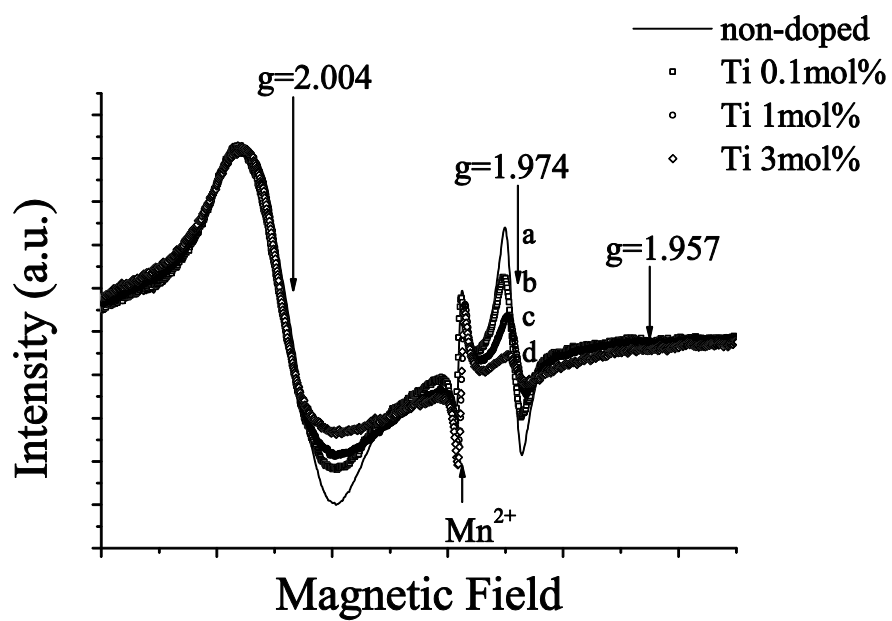


Figure 4.5. ESR spectra of (a) non-doped, (b) 0.1 mon% Ti-doped, (c) 1 mol% Ti- doped, and (d) 3 mol% Ti-doped BaZrO₃.

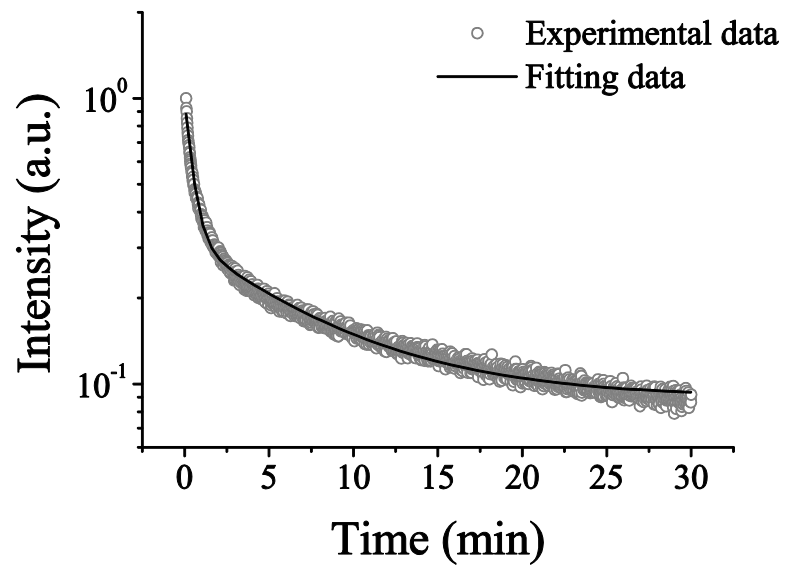


Figure 4.6. Long-lasting phosphorescence decay curve of BaZrO₃:Ti (0.2 mol%). The circles represent the experimental data and the solid line is the fitting result.

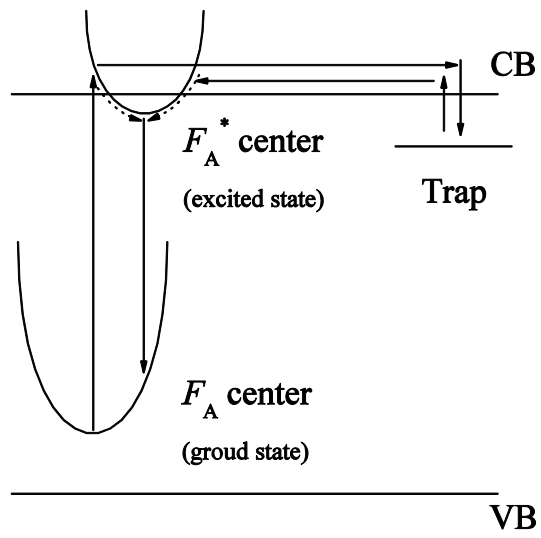


Figure 4.7. Schematic illustration of possible LLP mechanism for Ti-doped BaZrO₃.

violet-blue PL observed from the prepared Ti-doped BaZrO₃, since the luminescence of Ti³⁺ in BaZrO₃ can be red or near infrared even if detectable. Zero-phonon line is at around 616 nm in Ti³⁺ in sapphire, Al₂O₃ [15], in which crystal field strength can be larger than in BaZrO₃. In other words, the emission wavelength of Ti³⁺ in BaZrO₃ can be longer than 616 nm.

Lifetime of LLP was also evaluated. Figure 4.6 shows the LLP decay curve of BaZrO₃:Ti (0.2 mol%) and curve fitting result on the decay profile. The decay profile was not fitted by one exponential component, but well fitted by the sum of two exponential components [16, 17]:

$$I = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2), \quad (1)$$

where I is the phosphorescence intensity at time 't' after stopping the UV irradiation, A_1 and A_2 are constants, τ_1 and τ_2 are the decay times for the exponential components. The derived decay times and initial intensities for various amounts of doped TiO₂ were shown in Table 1. Decay time became shorter as the amount of TiO₂ increased. Particularly, in more than 1 mol% of TiO₂, decay time drastically decreased. In BaZrO₃:Ti (0.2 mol%), blue LLP can still be seen with the naked eye in the dark for 30 minutes or more after stopping UV irradiation, in the irradiation condition: UV lamp (245 nm, 513 $\mu\text{W}/\text{cm}^2$) for 30 seconds.

A possible LLP mechanism is as follows (Fig. 4.7). F_A centers are excited by UV light, and a part of excited F_A centers decays radiatively soon, and another part of them releases their electron into the conduction band of BaZrO₃. Then, Zr⁴⁺ and/or oxygen vacancies trap the released electrons, becoming to Zr³⁺, F^+ center or F center. The derived Zr³⁺ and F^+ center may be in an intermediate state but they can exist for a certain time, since Zr³⁺ and F^+ center intrinsically exist; however, the trapped electron is thermally detrapped at room temperature. Finally, an excited F_A center is reproduced by the detrapped electron, emitting

blue PL specific times after UV irradiation.

Amount of doped TiO ₂ (mol%)	Initial intensity (a.u.)	Decay times (s)	
		τ_1	τ_2
0.05	14232	29	395
0.2	12441	16	339
1	2293	6	44

Table 1 Decay times of BaZrO₃ for various amounts of doped TiO₂ by a curve fitting technique.

4.4. Conclusion

We synthesized Ti-doped perovskite-type oxide, BaZrO₃ by a solid-state reaction, and observed blue photoluminescence (PL) and long-lasting phosphorescence (LLP) from this material. Luminescence centers of PL and LLP are expected to be the same from the PL and LLP spectra, and F_A center, i.e., the defect pair of F^+ center and Ti^{3+} is a possible candidate. The peak wavelength and intensity of PL were influenced by the amount of additive TiO₂. Blue LLP was seen with the naked eye in the dark for 30 minutes after removal of 254 nm UV irradiation.

4.5. References

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Summary

In the present thesis, we utilized femtosecond laser for micro processing an internal area of sapphire. We introduced nanometer-scale defects inside sapphire using focused femtosecond laser pulses and investigated the behaviors of the defect formation. After laser irradiation, we examined the effect of the heat treatment on the defect structures induced by laser irradiation. The morphological changes of the defect structures after the annealing and its mechanism are discussed. Also, we aimed for the fabrication of two-dimensional nanometer-scale structures inside sapphire which have unique behaviors as compared with bulk sapphire. The results obtained are summarized as follows.

In chapter 1, the concept of femtosecond laser, a new regime of light – matter interactions are reviewed. The current state and future perspective of the femtosecond laser applications and efforts in the development of new materials are described.

In chapter 2, we have investigated the deformation mechanism of ruby in a microscopic area using a femtosecond laser having a pulse width, wavelength, and repetition rate of 238 fs, 780 nm, and 1 kHz, respectively. Transmission electron microscope (TEM) observation revealed that a specific oblique pattern originating from cracks having a width of approximately 10 nm formed at the focal point. The peak shift of ruby fluorescence indicated the existence of a residual stress of 0.11 GPa at the irradiated area. Considering the pattern and magnitude of the residual stress at the focal point, we suggest that the crack propagated along the $\{1\bar{1}02\}$ rhombohedral planes and the $\{1\bar{1}00\}$ planes by laser irradiation.

In chapter 3, we report on the fabrication of periodic array of dislocations and nanometer-scale pores within sapphire using femtosecond laser irradiation and subsequent annealing.

The dislocations and the nanometer-scale pores were aligned along the $\{1\bar{1}02\}$ and the $\{1\bar{1}00\}$ planes at intervals of 230 ~ 300 nm. The morphology of the nanometer-scale structures depend on the crystallographic orientation and the distance from the center of the focal point. The periodic nanometer-scale structures were formed through successive process: 1) formation of the amorphous phase and the cracks having a width of 30 nm by femtosecond laser irradiation. 2) the recrystallization of the amorphous phase, the thermally activated crack healing, and the relaxation of residual stress around the photomodified area by the heat treatment.

In chapter 4, long-lasting phosphorescence was observed from Ti-doped BaZrO_3 perovskite synthesized by a solid-state reaction. The phosphorescence color is blue and the phosphorescence can still be seen with the naked eye in the dark for 30 minutes or more after stopping UV irradiation. By the measurements of electron spin resonance (ESR) spectra, it was confirmed that F^+ center and Zr^{3+} exist in non-luminescent undoped BaZrO_3 and their concentrations decreased with the additive amount of TiO_2 . It is expected that the luminescence center is F_A center composed of Ti^{3+} and F^+ center.

List of Publications

Chapter 1

“Nanocrack propagation inside ruby single crystal by femtosecond laser irradiation”

C.W. Moon, S. Kanehira, M. Nishi, K. Miura, E. Tochigi, N. Shibata, Y. Ikuhara, K. Hirao
Proceedings of the 25th International Japan-Korea Seminar on Ceramics, 237-240 (2008)

Chapter 2

“Crack propagation in a ruby single crystal by femtosecond laser irradiation”

C.W. Moon, S. Kanehira, M. Nishi, K. Miura, T. Nakaya, E. Tochigi, N. Shibata, Y. Ikuhara, K. Hirao
Journal of the American Ceramic Society, in press (2009)

Chapter 3

“Dislocation Arrays in Sapphire using Femtosecond Laser Irradiation”

Chiwon Moon, Shingo Kanehira, Kiyotaka Miura, Eita Tochigi, Naoya Shibata, Yuichi Ikuhara and Kazuyuki Hirao
Proceedings of Materials Research Society, 2009 Fall Meeting, in press (2009)

“Periodic Array of Nanometer-Scale Pores inside Sapphire via Femtosecond Laser Irradiation and Subsequent Annealing”

C.W. Moon, S. Kanehira, M. Nishi, K. Miura, E. Tochigi, N. Shibata, Y. Ikuhara, K. Hirao
to be submitted

Chapter 4

“Optical properties of Ce^{3+} -doped Ordered $\text{Ba}_2\text{LnTaO}_6$ (Ln=Y, Gd, La) Perovskites”

C.W. Moon, M. Nishi, K. Miura, K. Hirao
Proceedings of the 22nd International Japan-Korea Seminar on Ceramics, 481-484 (2005)

“Tiを添加したペロブスカイト型酸化物BaZrO₃の青色長残光特性”

C.W. Moon, M. Nishi, K. Miura, K. Hirao

Journal of the Japan Society of Powder and Powder Metallurgy, 55, 201 (2008)

“Blue long-lasting phosphorescence of Ti-doped BaZrO₃ perovskites”

C.W. Moon, M. Nishi, K. Miura, K. Hirao

Journal of Luminescence, 129, 817-819 (2009)