Directionally controlled 3D ferroelectric single crystal growth in $LaBGeO_5$ glass by femtosecond laser irradiation

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Abstract: Laser-fabrication of complex, highly oriented three-dimensional ferroelectric single crystal architecture with straight lines and bends is demonstrated in lanthanum borogermanate model glass using a high repetition rate femtosecond laser. Scanning micro-Raman microscopy shows that the c-axis of the ferroelectric crystal is aligned with the writing direction even after bending. A gradual rather than an abrupt transition is observed for the changing lattice orientation through bends up to ~14°. Thus the single crystal character of the line is preserved along the bend through lattice straining rather than formation of a grain boundary.

OCIS codes: (220.4000) Microstructure fabrication; (220.4610) Optical fabrication; (050.6875) Three-dimensional fabrication; (320.2250) Femtosecond phenomena

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1. Introduction

Crystallization of glass by high repetition rate femtosecond (fs) laser irradiation is a novel method recently recognized for fabricating dots, waveguides, gratings, and frequency conversion elements for ultra-high density compact integrated optical and photonic devices [1–4], laser display [2], and optical memory systems [2]. The nonlinear nature of fs laser absorption allows for space-selective local heating and crystallization inside bulk glass, thus providing complete three dimensional (3D) control for creating the desired device element. Femtosecond laser crystallization has been reported in several systems [1–7], including the formation of single-crystal features [4]. However, little is known about the relationship between lattice orientation and line writing direction, in particular what happens when writing direction is changed. Assuming single crystal growth during the motion of the laser in a straight line, there are three possibilities for the growing crystal's reaction to a change in writing direction: In Fig. 1(a) the orientation of the lattice (indicated by arrows) does not change when the crystal growth direction is altered at the bend. Alternatively, the lattice orientation may turn to follow the growth direction, as in Fig. 1(b). Obviously, in this case the lattice is strained in the bend region so long as no grain boundary is formed at the bend, as in Fig. 1(c). Distinguishing which of these three cases occurs and whether this can be controlled is critical for the realization of functionalized single-crystals architectures. In particular, phase matching conditions for nonlinear optical applications of ferroelectric crystals in glass will be strongly influenced.

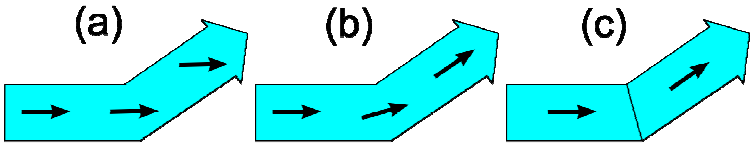

Fig. 1. Effect of bending if lattice orientation is fixed with respect to (a) sample, and (b) writing direction. While (a) may be expected, results show that (b) occurs instead. The orientation change could occur by lattice strain or by a grain boundary.

For 2D crystal growth at the glass surface using a continuous-wave (cw) laser and the barium bismuth borate material system, a correlation between growth direction and lattice orientation was found [8,9]. In these reports, it was speculated that the lattice changes continuously when the crystal growth direction is changed by altering the direction of the moving beam. In this work, we address these issues for quite different 3D-growth conditions under fs-laser irradiation, using a model glass system and exploiting scanning micro-Raman microscopy to characterize the lattice orientation of crystal lines inside the glass.

Lanthanum borogermanate ($LaBGeO_5$) is a model system for understanding the formation of anisotropic crystals from glass for several reasons. Unlike commonly used ferroelectric oxides such as $BaTiO_3$ or $LiNbO_3$, it forms glass easily. Upon heating $LaBGeO_5$ crystallizes congruently, avoiding complications from compositional variations during devitrification. In crystalline form, it is a ferroelectric below 530 °C with favorable nonlinear optical and electro-optical properties [10]. Recently, Gupta et al. succeeded in writing single crystal lines near the surface of an isostructural analog, $La_{0.5}Sm_{0.5}BGeO_5$ glass, with a cw 1064 nm

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Nd:YAG laser [11]. The present study extends the scope of this work from near-surface cw crystallization to 3D crystallization by exploiting the unusual nonlinear absorption of fs laser.

2. Experiment

The $LaBGeO_5$ glass was prepared by conventional melt-quenching. Stoichiometric amounts of La_2O_3 (99.99%), H_3BO_3 (99.99%) and GeO_2 (99.95%) were weighed to provide 40-gram batches. The powders were mixed for at least 2 hours and melted in a platinum crucible at 1250°C for 30 minutes. The melt was poured into a stainless steel mold and pressed with a steel plate, which were heated to ~400°C to reduce thermal shock. Glass pieces thus obtained were annealed for two hours near the glass transition temperature (T_g ~670 °C) [12]. Absence of residual stress was confirmed using crossed polarizers. Samples were then ground flat and one side was polished optically smooth with CeO_2 abrasive powder.

A 250 kHz, 800 nm regeneratively amplified Ti:Sapphire laser with 70 fs mode-locked pulses (Coherent, Inc.) was used as a light source for the irradiation experiments. The beam was focused through an optical microscope with a 50x objective lens and numerical aperture of 0.55. The microscope was equipped with a camera and spectrometer to allow direct observation of the sample during irradiation, including the 400 nm emission that is produced through frequency doubling, or second harmonic generation (SHG), of the incident 800 nm light once crystallization occurs. This property of nonlinear optical crystals was a useful indicator that non-centrosymmetric crystals had formed.

3. Results and discussion

Femtosecond laser crystallization relies primarily on localized heating. The ultrafast laser pulses deposit large amounts of energy into the glass at the focal point through nonlinear multiphoton absorption, and heat accumulation occurs at high repetition rates as new pulses arrive before the energy of previous pulses has had time to fully dissipate [13]. This localized heating allows for space-selective crystallization.

For the formation of the initial seed in our glass, samples were irradiated at room temperature. When focusing deep within the glass, 400-500 μm below the surface, crystallites consistently formed in the vicinity of the focal point within about 10 seconds. Interestingly, and in contrast to the congruent devitrification shown when using furnace heat [14] or CW laser beam [11], an unidentified phase formed first in the present experiments. If irradiation was continued at the same spot, a $LaBGeO_5$ seed appeared about one minute later (the two were readily distinguished by their Raman spectra, SHG intensity, and growth characteristics). Preliminary electron probe microanalysis (EPMA) results suggested that the local composition of the glass was altered by the laser, and that the unidentified intermediate phase was La-rich and B-depleted with respect to the bulk glass. This redistribution of elements was presumably driven by the laser-induced temperature gradient [15], as well as the charge displacement that developed as ponderomotive forces drove electrons away from the center of the high-energy pulses [16].

Once a $LaBGeO_5$ seed crystal was established, lines could be written in 3D by moving the sample stage in the X, Y, or Z directions. It is similar to the classic zone melting process for growing single crystals, but extended to three dimensions. Although the unidentified phase appeared quickly, it grew much more slowly than the $LaBGeO_5$ crystal, so after a short distance only $LaBGeO_5$ remained in the lines even though both phases were present in the seed. The lines tended to crack during writing at room temperature, but this could be prevented by holding the sample at elevated temperature during writing while using an appropriate laser power and writing speed. Lines could be written at speeds up to approximately 45 μm/s without outpacing the crystal. However, rather surprisingly, there was a minimum speed for single crystal formation. Below about 20 μm/s, severe cracking occurred at the focal point despite sample heating, resulting in disrupted crystal growth and the formation of polycrystalline lines. This is in direct contrast with the observations of Gupta et al. [11], who reported optimum single crystal line formation at a writing speed of 1 μm/s in an isostructural system, using cw rather than fs laser. The unusually high growth rate with fs

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laser crystallization may be related to higher temperatures near the focal point, but it remains unclear why low writing speeds increased cracking so substantially. The cracking likely involves stresses that arise from the thermal expansion mismatch and density difference between the glass and crystal, which would increase as writing speed is reduced due to higher peak temperatures and larger crystallized volumes.

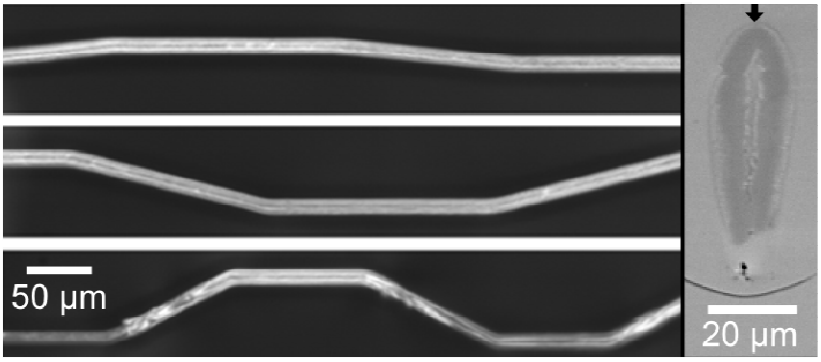

Fig. 2. Left: Polarized light micrographs of fs laser-crystallized $LaBGeO_5$ lines written in XY plane with bends of 6°, 14°, and 27°. Right: SEM backscattered electron image of a line cross-section. Arrow indicates incident beam direction.

Using the stage-control software, lines could be written with bends at various angles. Polarized light micrographs of crystal lines with bends at three angles are shown in Fig. 2. These lines were written at 20 µm/s in the XY plane 100 µm below the surface of a sample held at 400°C, with an average laser power of 300 mW. Bends of 6° and 14° did not cause obvious disruption, but a change in direction by 27° was enough to create significant inhomogeneities in the birefringence, likely due to thickness variation. A dark line is also visible near the center of all the lines. Examination of line cross-sections with SEM revealed a thin region in the middle of the otherwise continuous crystal which seemed to remain glassy. It appears that the peak temperature at the center of the heated volume becomes too high for crystallization, exceeding the melting temperature, so the crystal grows at the periphery rather than at the center of the fs laser beam. This explanation is supported by the results of Sakakura et al. [17], who calculated the temperature profile for 250 kHz fs laser irradiation of a soda lime silicate glass. They show a sharp and steep temperature profile with peak temperatures reaching thousands of °C. Despite these high temperatures, the heated volume is small enough that it is quenched quickly and vitrifies again as the focal point moves away, leaving glass at the crystal's center. This effect was reduced somewhat by varying irradiation conditions, and we suspect it could be avoided completely by manipulating the temperature gradient and reducing the peak temperature, perhaps by focusing less tightly and using a higher repetition rate with a lower energy per pulse.

Micro-Raman spectroscopy was used to confirm the identity of the crystalline phase and to characterize the lattice orientation of the lines. Spectra are shown in Fig. 3 for two orthogonal orientations, which agree well with the literature for Raman spectra of single crystal $LaBGeO_5$ [18,19]. In both cases, the Raman excitation and emission polarizations are parallel to each other; in spectrum (a) they are parallel to the crystal line while in (b) they are perpendicular to the crystal line. The same spectra could be obtained by holding the polarizations fixed and rotating the line by 90°, indicating that a change in lattice orientation will cause a change in the Raman spectrum for a given polarization. These spectra remained consistent across the length and width of all the lines investigated under both parallel and orthogonal Raman polarizations, including lines that were written in different directions, grown from different (presumably randomly oriented) seed crystals at different places in the sample, or even grown orthogonally from other lines acting as seeds. Such consistency of Raman spectra, considered together with the observed relationship between spectrum and orientation illustrated in Fig. 3, leads to the following three conclusions: (1) The lattice of each line is uniformly oriented (i.e.

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single crystal); (2) the lattice orientation is the same with respect to the direction of line writing for every line; and therefore, (3) changing writing direction to create bends, curves, or junctions in a crystal line causes a change in lattice orientation. Thus the scenario in Fig. 1(a) does not occur. Whether the mechanism of this orientation change is like Fig. 1(b) or Fig. 1(c) is important since it should affect the optical performance of the lines.

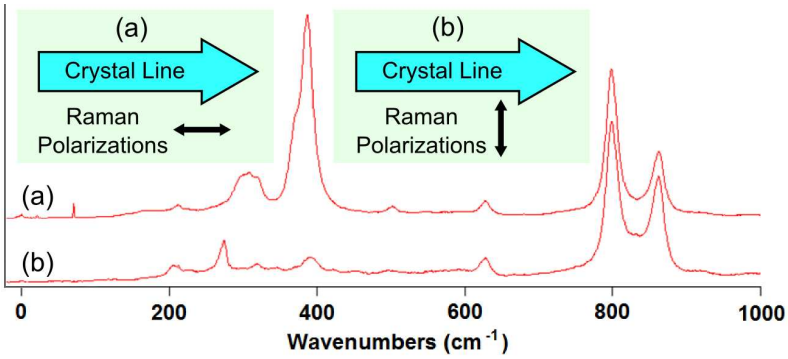

Fig. 3. Typical Raman spectra when excitation and emission polarizations are (a) parallel to a crystal line, and (b) orthogonal to a crystal line.

A more detailed analysis of the features of these Raman spectra offers more specific insights. Clearly, the most dramatic change in the Raman spectra in Fig. 3 is in the 392 cm^{-1} peak. Raman studies on single crystal $LaBGeO_5$ [18,19] show that this peak appears as the dominant peak only when the Raman polarizations are both parallel to the crystal's polar c-axis. As this peak is maximized in the present study when the Raman polarizations are parallel to the crystal lines, we conclude that the $LaBGeO_5$ crystal lattice always orients with the c-axis parallel to the line writing direction.

Turning our attention to the behavior of the lattice orientation at a bend of the crystal line, in Fig. 4 we map the intensity of the 392 cm^{-1} Raman peak using scanning micro-Raman microscopy. The left image demonstrates the feasibility of the technique, with intensity varying by a factor of 3 between two orthogonal lines (when the difference in orientation is maximized). The right image of a 14° bend shows a gradual increase in intensity from left to right, manifesting as a brightening of the crystal line from yellow (where the angle of the crystal line deviates from the horizontal Raman polarizations) to white (where the crystal line and Raman polarizations are nearly parallel). Since the intensity correlates directly with the lattice orientation when the polarization is fixed, the observed variation of intensity indicates that the lattice orientation also changes gradually, by lattice strain rather than an abrupt grain boundary, preserving a single crystal nature as the lattice rotates to accommodate the new line direction. The reduced intensity in the center of the crystal line may be attributed to the glassy core. The presence of glass in the interior and around the crystal line may help to dissipate stress from the rotation of the lattice and thus retard the formation of a grain boundary.

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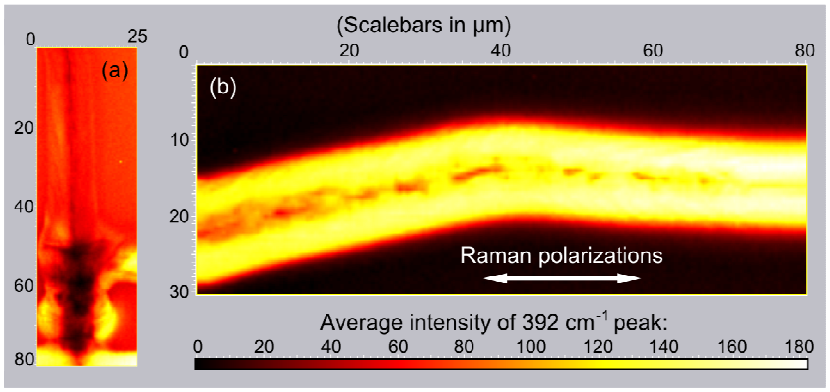

Fig. 4. Scanning Raman images of the average intensity of the 392 cm^{-1} Raman peak (resolution is 2 data points per micron). Image (a) demonstrates sensitivity of the technique: The yellow (light) colored region at the bottom is an existing line from which a new line was written orthogonally and developed a red color nearly the same as the surrounding glass (the dark region shows the effects of cracks due to low writing speed). Image (b) shows a gradual intensity increase across a 14° bend, indicating a gradual lattice reorientation in response to the change in writing direction.

The usual models of crystal growth by laser irradiation begin with the formation of polycrystalline seed, followed by the growth of the most favorably oriented grain. However, the present results suggest that crystal growth can proceed even from an unfavorably oriented seed as the lattice will adapt to the direction of laser writing anyway.

4. Conclusions

In summary, our studies of the fs-laser induced crystal growth in the $LaBGeO_5$ model system show: (1) The crystal's polar c-axis aligns with the growth direction as determined by the motion of the laser; and (2) the lattice orientation changes continuously throughout a bend. These detailed results are in agreement with those of Komatsu et al. [8,9] for the case of cw laser writing and demonstrate that, despite the lattice orientation being connected to the line writing direction, a gradual reorientation of the crystal lattice without creating grain boundaries is possible if bending angles are not too large. Since the same kind of reorientation after bending was also seen in cw laser crystallization with a different system, this is probably a more general characteristic of laser writing of single-crystal lines, which may manifest in laser crystallization of a wide range of systems.

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