Gadolinium molybdate, $\beta '$-(Sm,Gd)$_2$(MoO$_4$)$_3$ (GMO) is a unique crystal possessing both ferroelectricity and ferroelasticity, and there have been many reports on the phase transition behavior, structure, and optical properties of GMO crystals.$^{1-5}$ As a feature of ferroelasticity, GMO crystals have domain structures in which the direction of spontaneous polarization changes periodically depending on the domain structure. It is proposed from polarized micro-Raman scattering spectra and the azimuthal dependence of SH intensities that the orientation of (MoO$_4$)$_{2-}$-tetrahedra in GMO crystals changes gradually and periodically along the crystal line growth direction due to the spontaneous strains in GMO crystals. © 2009 American Institute of Physics. [DOI: 10.1063/1.3086725]
direction. The width of these lines is about 4 μm. The color is not uniform over the whole region of the lines as shown in Fig. 1. That is, the bright region (length is ~22 μm) and dark region (length is ~7 μm) periodically appeared, indicating that a periodic structural change with different refractive indices is formed along the laser scanning direction in the lines. Here, the periodic structural change shown in Fig. 1 is proposed to call "self-organized periodic domains."

The micro-Raman scattering spectra at room temperature for the bright and dark regions (Fig. 1) in the lines patterned by laser irradiations are shown in Fig. 2. It is seen that both regions give several sharp peaks at 325, 386, 746, 824, 851, 945, and 961 cm⁻¹. Considering the Raman scattering spectra for GMO or β'-Sm₂(MoO₄)₃ crystals reported so far, the peaks shown in Fig. 2 are assigned to the ferroelectric/ferroelastic SGMO crystalline phase having the orthorhombic structure of Pba₂. Nakajima et al. clarified that the ratio of Sm³⁺/Gd³⁺ in SGMO crystals formed in xSm₂O₃–(21.25–x)Gd₂O₃–63.75MoO₃–15B₂O₃ glasses (0 ≤ x ≤ 21.25) corresponds to that in the precursor glasses. It is, therefore, considered that the chemical composition of SGMO crystals in the patterned lines (Fig. 1) would be close to Sm₀.₂₅Gd₁.₇₅(MoO₄)₃. Furthermore, the x-ray diffraction (Cu Kα radiation, room temperature) pattern for the bundle (eighty) of crystal lines showed peaks corresponding to the {111} and {222} planes of β'-Sm₂(Gd,MoO₄)₃ crystals.

It is known that three different types of (MoO₄)₂⁻ tetrahedra having different mean distances of Mo–O bonds are present in GMO crystals, i.e., type-I, II, and III. Three crystallographically independent (MoO₄)₂⁻ tetrahedra form successive layers along the c-axis. Each (MoO₄)₂⁻ tetrahedron is discrete, and each oxygen atom in (MoO₄)₂⁻ is bonded only to one Mo atom, in addition to either one or two Gd atoms. All peaks that appeared in the Raman scattering spectra (Fig. 2) are assigned to the bending or stretching vibrations in Mo–O bonds in (MoO₄)₂⁻ tetrahedra. That is, the peaks at 325 and 386 cm⁻¹ are assigned to the bending modes of Mo–O bonds; the peaks at 746 and 851 cm⁻¹ are due to the antisymmetric Mo–O stretching vibrations in type-II or type-III; the peak at 824 cm⁻¹ is due to the antisymmetric Mo–O stretching vibrations in type-I; and the peaks at 945 and 961 cm⁻¹ are assigned to the symmetric Mo–O stretching vibrations in type-I and type-II or type-III, respectively. As seen in Fig. 2, the relative intensity of the peaks at 386 and 851 cm⁻¹ in the dark region is large compared with the spectra in the bright region. The Raman scattering spectra shown in Fig. 2, therefore, suggest that the orientation of SGMO crystals in the bright region, in particular the orientation of (MoO₄)₂⁻ tetrahedra in SGMO crystals, might be different from that in the dark region.

The photograph for the SHG microscope observation for the line is shown in Fig. 3. Second harmonic (SH) waves are detected from the line. It should be pointed out that the intensity of SH waves changes periodically depending on the positions of the line. That is, SHGs are observed in the bright regions appeared in the polarized optical photograph, but the dark regions gives extremely weak SH intensities. Furthermore, in particular, the center part in each bright region gives weaker SH intensity compared with the surrounding side parts. It is suggested that the orientation of SGMO crystals might change even in the bright region itself.

The azimuthal dependence of SH intensities for the line patterned by laser irradiations (P=1.2 W, S=5 μm/s) is shown in Fig. 4. The notations of H-H and H-V mean that the polarized electric field of the incident laser is parallel or perpendicular to the electric field of SH waves in the measurements, respectively. Furthermore, the rotation angles of 0° and 180° in the experiments correspond to the configuration that the polarized electric field of the incident laser is perpendicular to the line growth direction, and the rotation angles of 90° and 270° mean that the polarized electric field of the incident laser is parallel to the line growth direction. As seen in Fig. 4, the SH intensities change depending on the rotation angle. In the H-H configuration, two clear peaks are observed at the angles of θ₁~135° and θ₂~315°, i.e., the...
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line growth direction, and this would give the self-organized shown in Fig.4. Even in the H-V configuration, the SH posed, giving the azimuthal dependence of SH intensities other words, it is considered that the SH waves generated from both bright and dark regions in the lines are superim-
posed, giving the azimuthal dependence of SH intensities shown in Fig. 4. Even in the H-V configuration, the SH intensities change depending on the rotation angle, although the peaks are broad. These data also suggest that the orien-
tation of SGMO crystals in the lines changes periodically. The angle of 45° seems to be a key point for understanding the azimuthal dependence of SH intensities shown in Fig. 4. Aizu et al.3 reported that the piezoelectric moduli of d_{36} and d_{312} in ferroelastic GMO crystals referred to the system of the coordinate axes resulting from the rotation of the a- and b-axes about the c-axis through 45°.

We measured polarized micro-Raman scattering spectra for the lines shown in Fig. 1 and found that the two dimensional mapping of Raman scattering intensities for the peak appeared at 824 cm\(^{-1}\) shows the pattern similar to the SHG pattern shown in Fig. 3.\(^{16}\) The peak at 824 cm\(^{-1}\) has been assigned to the antisymmetric Mo–O stretching vibrations in type-I.13–15 It is, therefore, considered that the orientation of three types of (MoO\(_4\))\(^{2-}\) tetrahedra in SGMO crystals in the patterned lines changes gradually and periodically along the line growth direction, and this would give the self-organized domain structure in the lines. Such gradual and periodic di-

rection changes of (MoO\(_4\))\(^{2-}\) tetrahedra might be induced due to the spontaneous strains in ferroelastic SGMO crystals. SGMO crystal lines were patterned at different scanning speeds (the power was fixed to P=1.2 W), and it was found that the degree of the periodicity of domain structures changes depending on the laser scanning speed.\(^{16}\) This means that the degree of the periodicity of domain structures in the patterned lines would be related to the crystal growth rate. Finally, it should be pointed out that no periodic domain structures have been observed in other nonlinear optical crystal lines patterned by laser irradiations,\(^{11,12}\) and thus it seems that the appearance of the periodicity shown in Fig. 1 would be typical for crystal lines consisting of ferroelastic SGMO crystals. It is suggested that the periodic domain structures shown in Fig. 1 would not arise from the periodic compositional changes in the lines.

In conclusion, we succeeded in patterning ferroelastic SGMO crystal lines showing periodic domain structures by irradiations of cw Yb:YVO\(_4\) lasers with \(\lambda=1080\) nm on the surface of 3SmO\(_3\)–18.25GdO\(_3\)–63.75MoO\(_3\)–15B\(_2\)O\(_4\) glass. It was clarified that the intensity of SH waves changes depending on the domain structure. From polarized micro-

Raman scattering spectra and the azimuthal dependence of SH intensities, it was proposed that the orientation of (MoO\(_4\))\(^{2-}\) tetrahedra in SGMO crystals changes along the crystal line growth direction due to the spontaneous strains in ferroelastic SGMO crystals.

This work was supported from the Grant-in-Aid for Scientific Research from the Ministry of Education, Science, Sports, Culture and Technology, Japan Grant No. 19206069.

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\(^{15}\) L. Guy and M. Denis, J. Raman Spectrosc. 37, 189 (2006).

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FIG. 4. Azimuthal dependence of the SH intensities for the patterned line. The notations of H-H and H-V mean that the polarized electric field of the incident laser is parallel or perpendicular to the electric field of SH waves in the measurements, respectively.

• H-H
• H-V

Intensity (arb. units)
0 120 240 360
Rotation angle (deg.)

Separation angle of \(\Delta \theta = \theta_2 - \theta_1 = 180°\), and two weak peaks appeared at \(\theta_1 \sim 45°\) and \(\theta_2 \sim 225°\), i.e., \(\Delta \theta = 180°\). It should be pointed out that the relations of \(\theta_1 = \theta_1 + 90°\) and \(\theta_2 = \theta_2 + 90°\) are present. As indicated in Fig. 3, the bright regions in the polarized optical photograph give more strong SH intensities compared with the dark regions. It is, therefore, considered that the SH waves having the peaks at \(\sim 135°\) and \(315°\) in Fig. 4 come from the bright regions in the line. On the other hand, the origin of the SH waves giving the peaks \(\sim 45°\) and \(\sim 225°\) would be the dark regions in the line. In other words, it is considered that the SH waves generated from both bright and dark regions in the lines are superim-
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