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Relaxation phenomena in second-order nonlinearity of thermally and optically poled Nb_2O_5–TeO_2 glasses

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Abstract

We report on relaxation of second-harmonic intensity for optically poled $15Nb_2O_5 \cdot 85TeO_2$ bulk glass as well as thermally/electrically poled $15Nb_2O_5 \cdot 85TeO_2$ bulk glass doped with Na^+. The second-order nonlinearity induced by the thermal poling is rather stable. The decay of second-harmonic intensity is barely observed at 50˚C at least 5 h after ceasing of thermal poling. The activation energy for relaxation of second-harmonic intensity obtained from temperature dependence of relaxation time is 77 kJ mol^{-1}, which is somewhat larger than the activation energy for $20WO_3 \cdot 80TeO_2$ glass doped with Na^+ reported previously by the present authors. For optical poling of the $15Nb_2O_5 \cdot 85TeO_2$ bulk glass, fundamental and second-harmonic waves from a nanosecond pulsed Nd : YAG laser were utilized to induce second-order nonlinearity in the $15Nb_2O_5 \cdot 85TeO_2$ glass. The magnitude of second-order nonlinearity is saturated after optical poling for about 400 s. The decay of second-harmonic intensity is very rapid compared with the case of thermal poling. We speculate that some charged defects formed by laser irradiation are responsible for the second-order nonlinearity induced by optical poling.

1. Introduction

These days there have been increased interests in photoinduced and electric field-induced change of electronic structure and resultant variation of properties in inorganic glass materials. In particular, considerable attention has been paid to poling-induced optical second-order nonlinearity of glass materials since the findings of second-harmonic generation (SHG) in laser-irradiated Ge-containing silica glass fibre [1, 2] and thermally/electrically poled bulk silica glass [3]. SHG in glass materials is an interesting phenomenon from a fundamental viewpoint considering that glass does not have a macroscopic inversion symmetry because it is an optically anisotropic matter. As for the mechanism of SHG in thermally/electrically poled silica glass, it is thought that a large internal electric field present in the depletion region near the anode-side glass surface is frozen after poling and the electric field gives rise to the second-order nonlinearity via $\chi^{(2)} = 3\chi^{(3)}E_{dc}$ process, where $\chi^{(2)}$, $\chi^{(3)}$, and E_{dc} are the second-order nonlinear susceptibility, the third-order nonlinear susceptibility, and the internal dc electric field, respectively [3]. The depletion region is formed by migration of impurity cations such as Na^+. Also, alternative situation concerning SHG-active region is attained

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depending on the glass component and poling condition [4, 5]. Calvez *et al* [4] observed SHG in both anode- and cathode-side surface regions in poled fused silica. Qiu *et al* [5] revealed a case that second-harmonic wave is generated in bulk as well as near-surface region in poled silica glass.

On the other hand, phase-matched SHG is observed in Ge-containing silica glass fibre, since third-order nonlinear optical process among fundamental and second-harmonic waves makes a periodic dc electric field within the fibre, and breaks the macroscopic inversion symmetry [6]. It is thought that the dc electric field is caused by the photovoltaic effect [7]. Besides, charged Ge-associated point defects created by photochemical reaction [8] are suggested to be an atomistic origin for internal electric field. The photoinduced SHG has been observed in bulk glasses such as Ce-doped PbO–GeO_2, BaO–B_2O_3–SiO_2, PbO–SiO_2, Bi_2O_3–B_2O_3–SiO_2, $GeAsS_3$, and so forth as well [9–13].

We have investigated second-order nonlinearity induced in thermally poled tellurite glasses [14]. The tellurite glasses are one of the promising optoelectronics materials because of their high refractive indexes and high third-order nonlinear optical susceptibilities as well as their usefulness as an optical amplifier [15, 16]. The large third-order nonlinear susceptibility may lead to large second-order nonlinearity according to the $\chi^{(2)} = 3\chi^{(3)}E_{\mathrm{dc}}$ process. We revealed correlation between glass transition temperature and optimum poling temperature, which gives rise to the maximum second-harmonic intensity, for several tellurite glasses [17, 18]. Also, we found large second-order nonlinearity in Na^+-doped WO_3–TeO_2 glass [19] and long relaxation time of second-harmonic intensity in ZnO–TeO_2 glass [20]. Recently, we examined SHG in thermally poled $15Nb_2O_5\cdot 85TeO_2$ glass doped with Na^+ and clarified microstructural change of glass surface by the poling [21]. Because the $15Nb_2O_5\cdot 85TeO_2$ glass was sandwiched in between two commercially available Na^+-containing borosilicate glass plates during thermal poling, migration of Na^+ ions from the borosilicate glass into the tellurite glass sample took place. The penetration of Na^+ from anode-side surface was confirmed and the concentration profile of Na^+ was estimated by x-ray photoelectron spectroscopy [21]. We suggested that Na^+ ion incorporated into the anode-side surface of the $15Nb_2O_5\cdot 85TeO_2$ glass was responsible for the formation of dc internal electric field, leading to the SHG. Also, we revealed that a cation with high valence state such as Nb^{5+} could migrate by poling even below the glass transition temperature. From a practical viewpoint, the information concerning the decay of second-harmonic intensity induced in poled glasses is important. In this paper, we carried out measurements on time variation of second-harmonic intensity in thermally poled $15Nb_2O_5\cdot 85TeO_2$ glass doped with Na^+. In addition, an attempt was made to realize photoinduced SHG in the bulk $15Nb_2O_5\cdot 85TeO_2$ glass. We report on the decay of second-harmonic intensity in the optically poled $15Nb_2O_5\cdot 85TeO_2$ bulk glass as well.

2. Experimental procedure

2.1. Sample preparation

Glass with $15Nb_2O_5\cdot 85TeO_2$ composition was prepared from reagent-grade Nb_2O_5 (99.9%) and TeO_2 (99.9%) powder. The raw materials were mixed thoroughly, and melted in a platinum crucible at 850˚C for 15 min in air. The melt was poured into a mold made of graphite and cooled to room temperature in air. The glass thus obtained was annealed for 15 min at 400˚C, higher by 20˚C than its glass transition temperature determined by differential scanning calorimetry (Rigaku, DSC-8230B), and was cut into a rectangular parallelepiped by means of a saw pasted with diamond powder. The glass samples were subjected to optical measurements after the surfaces were polished. The size of the glass sample was about 10 mm × 10 mm × 1 mm.

2.2. Measurements

In order to make the as-prepared tellurite glass SHG-active, the glass was thermally poled in air. The schematic illustration of the poling apparatus is shown in figure 1. The tellurite glass was sandwiched in between two commercially available borosilicate glass plates the thickness of which was 0.15 mm, and contacted with electrodes made of stainless steel. The borosilicate glass plates were used to avoid discharge between the electrodes and precipitation of metallic tellurium in the samples during the poling. The glass sample was heated to an aimed temperature (poling temperature) in an electric furnace. After a voltage of 3 kV was applied for 15 min with the temperature constant, the tellurite glass was cooled to room temperature with the voltage applied. The voltage was removed after the tellurite glass was cooled to room temperature. When Nb_2O_5–TeO_2 glasses were thermally poled by applying a voltage larger than 3 kV, discharge took place during poling, leading to precipitation of metallic tellurium. In order to avoid this phenomenon and perform systematic investigation of SHG at a wide range of elevated temperatures, a voltage of 3 kV was used.

The intensity of second-harmonic wave was measured by using the Maker fringe method [22]. A set up for the measurements is shown in figure 2. As a fundamental wave, the light at 1064 nm from a pulsed Nd : YAG laser (Spectra Physics, GCR-11), which operated in a Q-switched mode with 10 Hz repetition rate, was used. The p-polarized laser was incident on the poled glass sample, which was rotated around on axis parallel to the glass surface. The sample was placed in an electric furnace with silica glass optical windows for the SHG measurement at elevated temperatures. After

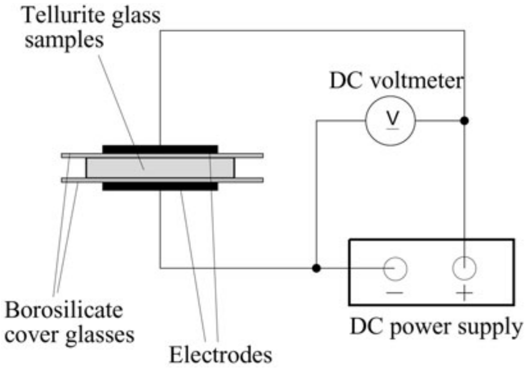

Figure 1. A schematic illustration of apparatus for thermal poling of $15Nb_2O_5\cdot 85TeO_2$ glass.

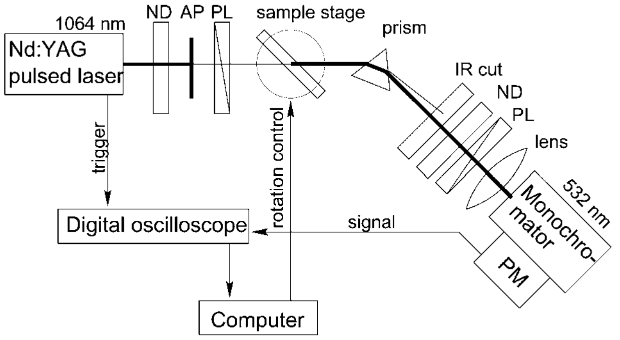

Figure 2. A schematic illustration of equipment for measurements of second-harmonic generation in thermally poled $15Nb_2O_5{\cdot}85TeO_2$ glass. The Maker fringe method was used for the SHG measurements. The abbreviations, i.e. ND, AP, and PL denote neutral density filter, aperture, and polarizer, respectively.

passing through IR cut filters, the output p-polarized light at 532 nm generated from the sample was detected by the use of a monochromator (Hamamatsu Photonics, R955) equipped with a photomultiplier. Y-cut quartz (1.046 mm thick) was used as a reference for the second-harmonic intensity.

Optical poling was carried out with fundamental and second-harmonic waves from a Q-switched Nd : YAG laser (Coherent, infinity 40–100). The pulse width and the repetition rate were 3 ns and 20 Hz, respectively. Both linearly polarized (s-polarized) fundamental and second-harmonic light beams were incident in direction perpendicular to the glass surface. After encoding of second-order nonlinearity in glass, the incident second-harmonic wave was turned off, and second-harmonic signal generated from the optically poled glass sample was detected by using a photomultiplier and an oscilloscope. The second-harmonic wave generated from the glass sample was s-polarized by passing through a polarizer. The second-harmonic intensity of Y-cut quartz 1 mm thick was also measured as a standard under the same conditions.

Optical absorption spectrum of the as-annealed glass sample was measured at room temperature using a spectrophotometer (Hitachi 330) to evaluate optical transitions in the $15Nb_2O_5{\cdot}85TeO_2$ glass.

3. Results

3.1. Thermal poling

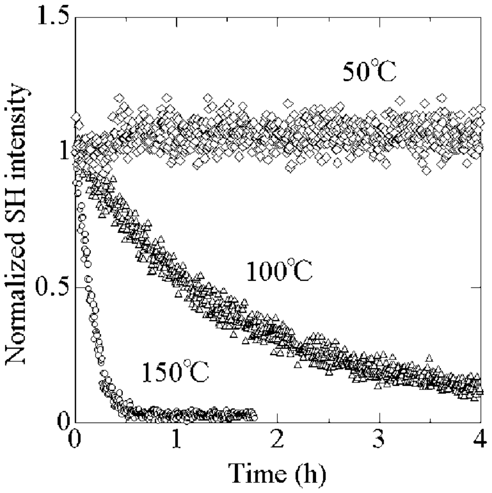

Figure 3. Decay of second-harmonic intensity for $15Nb_2O_5{\cdot}85TeO_2$ glass doped with Na^+. The glass was thermally poled at 260˚C. The measurements of decay were carried out at 50˚C (□), 100˚C (△), and 150˚C (○).

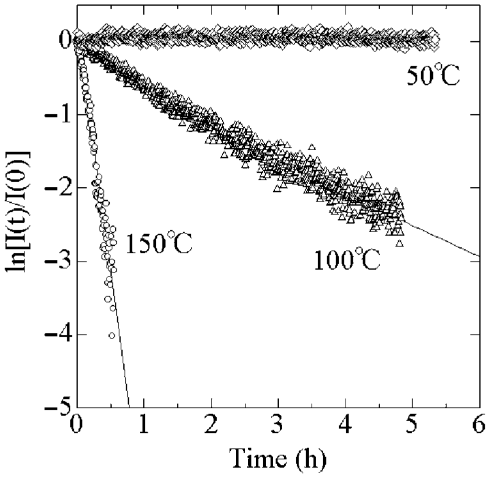

Figure 4. Decay of second-harmonic intensity for $15Nb_2O_5{\cdot}85TeO_2$ glass doped with Na^+ poled at 260˚C. In the ordinate, $\ln[I(t)/I(0)]$, where I is the second-harmonic intensity and t is the time after the ceasing of thermal poling, is shown. The measurements were carried out at 50˚C (□), 100˚C (△), and 150˚C (○). The solid curves were drawn by assuming that the data are expressed by the stretched exponential function (equation (1)).

Figure 3 shows the variation of second-harmonic intensity with time at various temperatures after poling at 260˚C. As reported previously, the second-harmonic intensity of the $15Nb_2O_5{\cdot}85TeO_2$ glass doped with Na^+ shows a maximum when the thermal poling is carried out at 260˚C. The values of temperature shown in figure 3 indicate the measurement temperature. The decay becomes more rapid as the temperature is increased, as naturally expected. The decay was barely observed at 50˚C within the measurement time of 5 h or so at least. In the ordinate of figure 4, $\ln[I(t)/I(0)]$, where $I(t)$ and $I(0)$ are second-harmonic intensities at t and 0 h after the ceasing of thermal poling, is shown for the Na^+-doped $15Nb_2O_5{\cdot}85TeO_2$ glass poled at 260˚C. The solid curves were drawn on the assumption that the decay is expressed by the stretched exponential function, i.e.

$$I(t) = I(0)\exp\left[-\left(\frac{t}{\tau}\right)^{\beta}\right], \tag{1}$$

where τ is the average relaxation time and β is the parameter representing the distribution of relaxation time. The stretched exponential function is useful to analyse a relaxation phenomenon governed by more than two kinds of relaxation components or a single component with finite distributions. The values of τ and β obtained from the analysis are summarized in table 1. The value of β varies from unity to 0.7.

The variation of relaxation time with temperature is shown in figure 5. The natural logarithms of inverse relaxation time

Table 1. Average relaxation time τ and parameter β in the stretched exponential function (equation (1)) for decay of second-order nonlinearity induced in Na^+-doped $15Nb_2O_5\cdot 85TeO_2$ bulk glass by thermal poling. The poling was carried out at 260°C.

Temperature (°C)	τ (h)	β
50	—[a]	—[a]
75	19	0.7
100	1.7	0.9
150	0.15	1

[a] The relaxation time could not be obtained because the decay was very sluggish at least 5 h after ceasing of thermal poling.

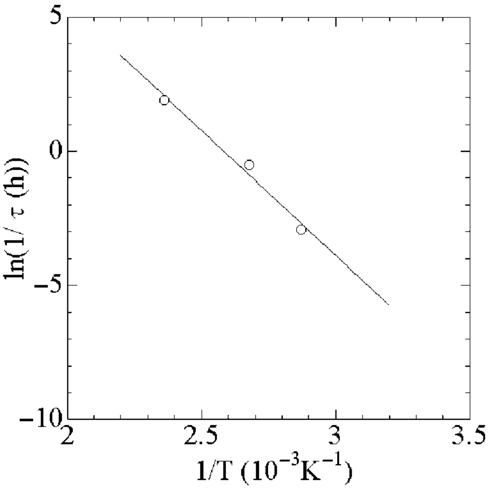

Figure 5. Temperature dependence of relaxation time for Na^+-doped $15Nb_2O_5\cdot 85TeO_2$ glass poled at 260°C. The straight line was drawn by the least-squares method.

and the inverse temperature are plotted in the ordinate and the abscissa, respectively. In figure 5, the solid line was drawn by fitting the relation

$$\frac{1}{\tau} = \left(\frac{1}{\tau_0}\right) \exp\left(\frac{-E}{RT}\right), \tag{2}$$

where T is the temperature, R is the gas constant, E is the activation energy, and τ_0 is a constant to the experimental data. From the slope of the line, $E = 77\,\mathrm{kJ\,mol^{-1}}$ was obtained.

3.2. Optical poling

Optical absorption spectrum of $15Nb_2O_5\cdot 85TeO_2$ glass before optical poling is shown in figure 6. Intense absorption is observed at a wavelength range shorter than about 420 nm. No distinct absorption bands are detected in a visible range longer than this wavelength. Figure 7 shows dependence of second-harmonic intensity on time for encoding of second-order nonlinearity. The closed and open circles reflect the difference in peak powers of pulsed fundamental (1064 nm) and second-harmonic (532 nm) waves used for encoding of second-order nonlinearity; the closed circles correspond to $1\,\mathrm{GW\,cm^{-2}}$ at 1064 nm and $4\,\mathrm{MW\,cm^{-2}}$ at 532 nm, and the open circles represent results obtained with $0.8\,\mathrm{GW\,cm^{-2}}$ at 1064 nm and $3\,\mathrm{MW\,cm^{-2}}$ at 532 nm. These peak powers are almost identical to those used for optical poling of Ce^{3+}-doped aluminosilicate glass fibre [23] and lower by one to two orders of magnitude than those for Ge-doped silica glass fibre [6] and GeO_2–SiO_2 bulk glass [11]. The second-harmonic intensity in the ordinate of figure 7 is normalized by the maximum intensity of second-harmonic wave generated from Y-cut quartz 1 mm thick. The intensity of second-harmonic wave generated from the optically poled $15Nb_2O_5\cdot 85TeO_2$ glass is apt to be saturated after poling for about 400 s. The saturated second-harmonic intensity is lower by four orders of magnitude than the second-harmonic intensity of Y-cut quartz. Because the second-harmonic intensity is rather low, the value in the ordinate involves large relative experimental errors mainly caused by fluctuation of laser power. The saturated second-harmonic intensity is larger for the glass poled with higher laser powers.

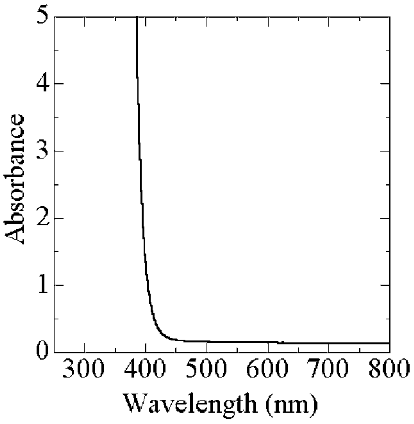

Figure 6. Room temperature optical absorption spectrum of $15Nb_2O_5\cdot 85TeO_2$ glass before optical poling.

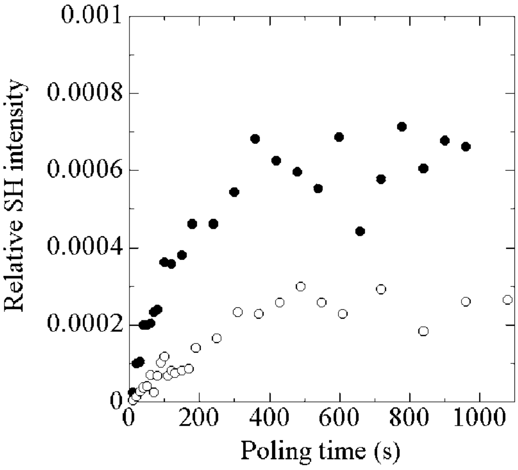

Figure 7. Dependence of second-harmonic intensity on duration for optical encoding of second-order nonlinearity in $15Nb_2O_5\cdot 85TeO_2$ glass. The closed and open circles correspond to the pulse peak powers of $1\,\mathrm{GW\,cm^{-2}}$ at 1064 nm and $4\,\mathrm{MW\,cm^{-2}}$ at 532 nm, and of $0.8\,\mathrm{GW\,cm^{-2}}$ at 1064 nm and $3\,\mathrm{MW\,cm^{-2}}$ at 532 nm, respectively. The second-harmonic intensity relative to the maximum intensity of second-harmonic wave generated from Y-cut quartz is shown in the ordinate.

The decay of induced second-order nonlinearity at room temperature is illustrated in figure 8. The closed and open circles in this figure correspond to the high and low pulse peak powers used for optical poling. In this figure, $\ln[I(t)/I(0)]$, where t denotes the time in seconds, is shown in the ordinate.

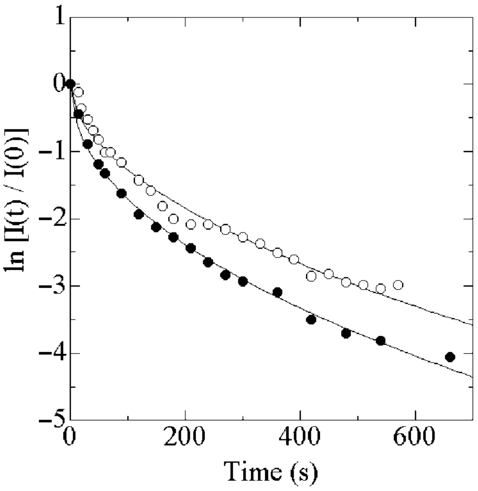

Figure 8. Decay of second-harmonic intensity of optically poled $15Nb_2O_5{\cdot}85TeO_2$ glass at room temperature. The closed and open circles correspond to the pulse peak powers of 1 GW cm^{-2} at 1064 nm and 4 MW cm^{-2} at 532 nm, and of 0.8 GW cm^{-2} at 1064 nm and 3 MW cm^{-2} at 532 nm, respectively. The solid curves were drawn by fitting the stretched exponential function to the experimental data.

Table 2. Average relaxation time τ and parameter β in the stretched exponential function (equation (1)) for decay of second-order nonlinearity induced in $15Nb_2O_5{\cdot}85TeO_2$ bulk glass by optical poling.

Pulse peak power for optical poling			
Fundamental (GW cm^{-2})	Second-harmonic (MW cm^{-2})	τ (s)	β
1	4	33	0.5
0.8	3	62	0.5

The solid curves were drawn using equation (1). The values of τ and β are summarized in table 2. The relaxation time is very short compared with those reported for optically poled GeO_2–SiO_2 [11] and Bi_2O_3–B_2O_3–SiO_2 glasses [12], but it has the same order as BaO–B_2O_3–SiO_2 glasses [10]. On the other hand, the values of β are almost identical to that of Bi_2O_3–B_2O_3–SiO_2 glasses, i.e. $\beta = 0.46$ [12]. Furthermore, the decay is more rapid in the glass for which higher pulse peak powers were used for poling and readout of SHG.

4. Discussion

For the second-harmonic intensity of thermally poled $15Nb_2O_5{\cdot}85TeO_2$ glass doped with Na^+, the decay rate at around room temperature is rather slow, although the decay becomes more rapid as the temperature is raised. The decay of second-harmonic intensity is barely observed at 50°C at least 5 h after ceasing of poling. Based on the extrapolation of the data at 75°C, 100°C, and 150°C, the relaxation time at 25°C, i.e. room temperature, can be estimated to be 1.3×10^3 h. This value is about 3 times as long as the relaxation time at room temperature for $20WO_3{\cdot}80TeO_2$ glass poled at 280°C, i.e. 4.0×10^2 h and longer by two orders of magnitude than that for $20WO_3{\cdot}80TeO_2$ glass poled at 260°C, i.e. 45 h [24]. The activation energy for the relaxation of second-harmonic intensity observed in the $20WO_3{\cdot}80TeO_2$ glass poled at 260°C is 47 kJ mol^{-1}. On the other hand, the activation energy for the present $15Nb_2O_5{\cdot}85TeO_2$ glass is 77 kJ mol^{-1} as mentioned above. The difference in activation energy between $15Nb_2O_5{\cdot}85TeO_2$ and $20WO_3{\cdot}80TeO_2$ glasses may be attributed to the difference in glass structure. The activation energy for dc conduction of Na^+ ion in $10Na_2O{\cdot}90TeO_2$ glass at 100–260°C is 102 kJ mol^{-1} [25], and the activation energy for viscous flow observed in $20Na_2O{\cdot}80TeO_2$ glass just above its glass transition temperature is 530 kJ mol^{-1} [26]. It is plausible that the relaxation of second-harmonic intensity in the $15Nb_2O_5{\cdot}85TeO_2$ glass doped with Na^+ is related with diffusion of Na^+ ions. The Na^+ ions that penetrate from the sodium borosilicate glass plate during the thermal poling are accumulated at the anode-side surface, and bring about SHG. At high temperatures, these Na^+ ions can diffuse so that the distribution of Na^+ ions becomes homogeneous inside the glass. We observed that second-harmonic intensity was drastically decreased when the anode-side glass surface was mechanically etched to 10 μm or so. Hence, it is thought that the SHG-active region is mainly restricted just below the glass surface contacted with the anode during the thermal poling.

The value of β depends on temperature at which the second-harmonic intensity decays as shown in table 2. The origins of β different from unity in the present case are a distribution of sites for diffusing species and/or interaction among those species; the diffusing species are presumably Na^+ ions. The parameter β becomes to be less than unity when a relaxation phenomenon is governed by more than two kinds of components or a single type of component with finite distributions of chemical potential. A strong affinity or repulsive force among components results in discrepancy of β from unity as well. The present result indicates that β is unity for the relaxation at higher temperatures, while β is smaller than unity at lower temperatures, as shown in table 1. This means that the distribution of relaxation time is broad at lower temperatures.

In comparison with the thermal poling, the decay rate is more rapid for optical poling. Although the atomistic origin and mechanism for the optically induced second-order nonlinearity in the $15Nb_2O_5{\cdot}85TeO_2$ bulk glass are unclear at this moment, they are presumably attributable to the photoinduced charged defects which were postulated for optically encoded second-order nonlinearity in several oxide glasses studied previously. It should be noted that doping of only 0.008 wt% of Ce^{3+} into aluminosilicate glass fibre gives rise to SHG as revealed by Krol and Simpson [23]. Since the purity of the raw materials, i.e. TeO_2 and Nb_2O_5 powder, is 99.9% as mentioned above, the concentration of impure multivalent ions possibly present in the $15Nb_2O_5{\cdot}85TeO_2$ glass may be comparable to the doping level of Ce^{3+} in the aluminosilicate glass fibre. In addition, Nb and Te are multivalent elements; Nb^{5+} and Nb^{4+} are relatively stable for Nb, and Te takes a variety of oxidation states such as Te^{6+}, Te^{4+}, and Te^{2-}. These ions can contribute to the formation of internal dc electric fields via photoionization and/or trapping of electrons. However, since there are no absorption peaks at 1064 and 532 nm as shown in figure 6, it is thought that the efficiency for the process of the formation of photoinduced charged defects is very low, leading to the low second-harmonic intensity.

The relaxation time for the induced second-order nonlinearity in the $15Nb_2O_5{\cdot}85TeO_2$ glass shown in table 2 is very short compared with other optically poled glasses such as GeO_2–SiO_2, Bi_2O_3–B_2O_3–SiO_2 and Ce^{3+}-doped aluminosilicate glasses. For instance, the relaxation time for optically induced second-order nonlinearity in Bi_2O_3–B_2O_3–SiO_2 glasses lies in the range of 1500–3000 min, i.e. longer by three orders of magnitude than the relaxation times of $15Nb_2O_5{\cdot}85TeO_2$ glass. On the other hand, the relaxation time for the $15Nb_2O_5{\cdot}85TeO_2$ glass is almost the same as those reported for optically poled PbO–SiO_2 glasses. The relaxation time varies from about 1.6–0.4 min as the concentration of PbO increases from 30 to 60 mol% in the optically poled PbO–SiO_2 glasses [10]. One possible explanation for the large difference in relaxation time between the present $15Nb_2O_5{\cdot}85TeO_2$ glass and other glasses such as GeO_2–SiO_2, Bi_2O_3–B_2O_3–SiO_2 and Ce^{3+}-doped aluminosilicate is the discrepancy in inherent lifetime or stability of photoinduced defects which contribute to the SHG; the lifetime of photoinduced defects may be much shorter in the $15Nb_2O_5{\cdot}85TeO_2$ glass than in the Bi_2O_3–B_2O_3–SiO_2 glasses. It is also possible that the relaxation of photoinduced defects to their original states is accelerated by the irradiation of the fundamental wave used for the observation of SHG. Si *et al* [11] observed that for optically poled $10GeO_2{\cdot}90SiO_2$ glass the second-harmonic intensity was kept constant when the measurement of SHG was restarted 10 h after the fundamental wave was turned off although the intensity decreased gradually during the irradiation with the fundamental wave for the SHG measurements. They concluded that the decay of second-harmonic intensity is mainly ascribable to the erasure of induced second-order nonlinearity by the fundamental wave irradiation. A similar phenomenon possibly takes place in the $15Nb_2O_5{\cdot}85TeO_2$ glass. In particular, the effect of heat to increase temperature in local area of the glass is significant because the nanosecond pulsed laser was used in the present case; an increase in temperature can accelerate the relaxation of electronic defects. This idea is coincident with the fact that the decay of second-harmonic intensity is more rapid for the irradiation with higher laser power as shown in figure 7 and table 2. Also, it should be noted that the fundamental wave with 27 MW cm^{-2} was used for the measurements of SHG in the Bi_2O_3–B_2O_3–SiO_2 glasses. This power is lower by two orders of magnitude than those used in the present study.

5. Conclusions

The thermally poled $15Nb_2O_5{\cdot}85TeO_2$ glass doped with Na^+ exhibits rather long relaxation time for second-harmonic intensity at around room temperature. The analysis of temperature dependence of relaxation time suggests that the migration of Na^+ ions incorporated into the $15Nb_2O_5{\cdot}85TeO_2$ glass by thermal poling is responsible for the decay of second-harmonic intensity.

In addition, the second-order nonlinearity was induced in $15Nb_2O_5{\cdot}85TeO_2$ bulk glass by optical poling with nanosecond pulsed lasers at wavelengths of 1064 and 532 nm, although the second-harmonic intensity decays very rapidly. The photoinduced second-order nonlinearity tends to be saturated after optical poling for about 400 s. We infer that the formation of dc electric field due to the photo-ionization of multivalent impurities, Nb^{5+} and Te^{4+}, is responsible for the phase-matched SHG.

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