Second-harmonic generation in optically poled tellurite glasses doped with V_2O_5

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Yoshinori Yonesaki[1]**, Katsuhisa Tanaka**[2,4]**, Jinhai Si**[3] **and Kazuyuki Hirao**[1]

[1] Department of Material Chemistry, Graduate School of Engineering, Kyoto University, Yoshidahonmachi, Sakyo-ku, Kyoto 606-8501, Japan
[2] Department of Chemistry and Materials Technology, Faculty of Engineering and Design, Matsugasaki, Sakyo-ku, Kyoto 606-8585, Japan
[3] Photon Craft Project, ICORP, JST, Keihanna-plaza, Super-laboratory 2-6, 1-7 Hikaridai, Seikacho, Kyoto 619-0237, Japan

E-mail: katsu@ipc.kit.ac.jp

Abstract

Second-harmonic generation (SHG) has been observed in optically poled tellurite glasses doped with V_2O_5. The optical poling has been performed by using the fundamental wave at the wavelength of 1064 nm and the second-harmonic wave at 532 nm from a Nd:YAG pulsed laser. The second-harmonic intensity of $15Nb_2O_5 \cdot 85TeO_2$ glasses containing V_2O_5 is larger by two orders of magnitude than that of tellurite glass of the same composition without V_2O_5. Electron spin resonance spectra indicate that vanadium ions are present as either V^{4+} or V^{5+}, and that the relative amount of V^{4+} is decreased when the glass is irradiated with second-harmonic waves of a Nd:YLF laser (523 nm) whose wavelength lies in the tail of the intense absorption mainly ascribable to charge transfer in the V^{5+}–O^{2-} bond. We propose a model in which a positive hole and an electron, generated by photo-oxidation of V^{4+} into V^{5+} due to two-step photon absorption at 532 nm, bring about a periodic arrangement of electric dipoles and/or periodic alternation of an internal dc electric field, resulting in optically induced SHG in the present tellurite glasses doped with V_2O_5.

1. Introduction

Tellurite glasses are promising optoelectronic materials due to their high refractive index and high transmittance in the infrared-to-visible region. Also, they are easy to fabricate because of their low melting temperature. We have tried to add second-order nonlinear optical properties, applicable in short-wavelength lasers, parametric multipliers, and so on,

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[4] Author to whom any correspondence should be addressed.

into tellurite glasses [1–7]. Because tellurite glasses have high refractive indices, they should possess large third-order nonlinear susceptibility $\chi^{(3)}$ according to Miller's rule. This suggests the possibility that tellurite glasses possess large second-order nonlinear susceptibility $\chi^{(2)}$ when the following relation is taken into account:

$$\chi^{(2)} = 3\chi^{(3)} E_{dc}. \tag{1}$$

Although materials such as glasses which have an inversion symmetry over the scale of the wavelength of light are not allowed to show second-order nonlinear optical phenomena, the procedure called 'poling' gives glasses macroscopic asymmetric structure potentially leading to second-order nonlinearity [8]. In the present study, we adopted optical poling to bring about second-harmonic generation (SHG) in tellurite glasses. Optical poling is a technique in which a periodic arrangement of electric dipoles or periodic alternation of an internal dc electric field is encoded inside a material by laser irradiation. Such a process gives rise to phase-matched SHG because the periodicity of the electric dipoles or electric field is relevant to the wavelength of the laser with which the material is irradiated. In fact, the optical poling process has been effectively applied to glass fibres and bulk glass materials [9–16]. It is possible to modify just the electronic structure of a localized region in glass by optical poling. This is useful for fabrication of optoelectronic devices such as optical memories and optical modulators.

What is important in realizing large second-order nonlinearity by optical poling is the selection of the composition of the glass. We have reported on SHG in optically poled $15Nb_2O_5 \cdot 85TeO_2$ glass [17]. Although the glass exhibited SHG after poling with laser beams at 1064 and 532 nm, the second-harmonic intensity was lower by four orders of magnitude than the intensity of α-quartz 1 mm thick. In addition, the decay of encoded second-order nonlinearity was as rapid as 30–60 s. In this study, we tried to carry out doping of transition metal ions and to modify the glass composition in order to improve the second-order nonlinear optical properties of the $15Nb_2O_5 \cdot 85TeO_2$ glass. We expected photo-ionization of transition metal ions to be induced, resulting in a large second-order nonlinearity in glasses containing the transition metal element. We used vanadium ions as the dopant because vanadium is in the same group of elements as niobium. Also, we modified the glass composition and electronic structure by adding K_2O. We performed optical absorption spectroscopy, SHG measurements, and electron spin resonance (ESR) spectroscopy to characterize the electronic state of the vanadium ions and to reveal the origin of the SHG induced by optical poling.

2. Experimental procedure

2.1. Preparation of samples

The glasses were prepared from reagent-grade Nb_2O_5, TeO_2, K_2CO_3, and V_2O_5. The purity of these raw materials is 99.9%. The glass compositions are summarized in table 1. The raw materials were mixed thoroughly, and melted in a platinum crucible at 850 °C for 90 min in air. The melt was poured onto a stainless steal plate, and cooled in air to obtain glass. The glass transition temperature was measured using differential scanning calorimetry (DSC, Rigaku, Thermal Analysis Station TAS100). After the glass was annealed at just above the glass transition temperature for 20 min, it was cooled down to room temperature. The annealed glass was cut into plates with a diamond-paste-coated saw. Both sides of the surfaces of the glass plate were polished with sandpaper and CeO_2 powder. The thickness of the glass samples was 1.00 ± 0.01 mm. The glass samples prepared were examined by optical absorption spectroscopy at room temperature. A spectrophotometer (HITACHI 330) was used for the measurements.
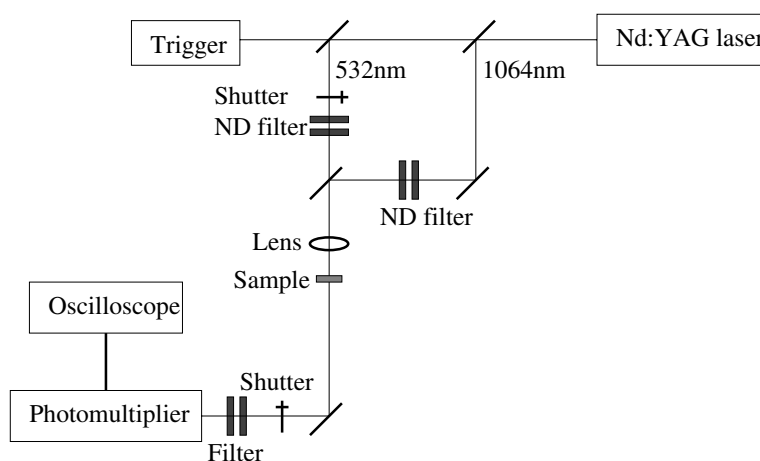
Figure 1. A schematic illustration of the set-up for optical poling and measurements of SHG. The seeding beams for encoding of SHG are fundamental (1064 nm) and second-harmonic (532 nm) waves of a pulsed Nd:YAG laser.

Table 1. Compositions of V_2O_5-doped tellurite glasses prepared in the present study.

Notation	Composition (molar ratio)			
	Nb_2O_5	TeO_2	K_2O	V_2O_5
	15	85		0.01
	15	85		0.03
	15	85		0.05
	15	85		1
NTK0	14.9	84.6		0.5
NTK3	14.5	82.0	2.99	0.5
NTK5	14.2	80.3	4.98	0.5
NTK7	13.9	78.7	6.97	0.5
NTK10	13.4	76.1	9.95	0.5
NTK15	12.7	71.9	14.9	0.5

2.2. Optical poling and SHG measurements

A glass sample was optically poled by irradiating it with both fundamental (1064 nm) and second-harmonic (SH wave, 532 nm) waves of a Q-switched Nd:YAG pulsed laser (COHERENT, infinity 40-100). A schematic illustration of the set-up for optical poling is shown in figure 1. The pulse width and the repetition rate for the pulsed Nd:YAG laser were 3 ns and 30 Hz, respectively. The incident beams used for poling are referred to as the 'seeding beams'. The seeding beams were focused on the vicinity of the glass surface, and the irradiation lasted for 10 min. The laser powers were 5.70 kW cm^{-2} at 1064 nm and 0.191 kW cm^{-2} at 532 nm for vanadium-doped $15Nb_2O_5 \cdot 85TeO_2$ glasses, and 143 W cm^{-2} at 1064 nm and 15.0 W cm^{-2} at 532 nm for vanadium-doped Nb_2O_5–TeO_2–K_2O glasses.

SHG measurements were carried out using the same set-up. After the seeding SH wave was shut off, only the fundamental wave, whose wavelength was 1064 nm, was incident on the glass sample. The intensity of the SH wave generated in the glass via second-order nonlinear optical process was detected by a photomultiplier connected with an oscilloscope.
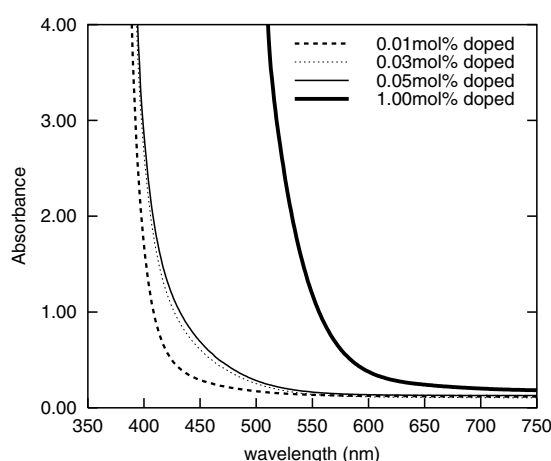
Figure 2. Optical absorption spectra for $15Nb_2O_5 \cdot 85TeO_2$ (mol%) glasses doped with V_2O_5. The concentrations of V_2O_5 were 0.01, 0.03, 0.05, and 1 mol%.

2.3. ESR spectroscopy

ESR spectra were obtained by using a commercial measurement system (Bruker, ESP300E) at room temperature. The frequency and the power of the microwaves were 9.626 GHz (X-band) and 1.00 mW, respectively. For $15Nb_2O_5 \cdot 85TeO_2$ glasses doped with vanadium, a bulk glass sample cut into rectangular parallelepipeds was put into a silica tube. This tube was set into a holder with a hole through which a cw Nd:YLF laser beam could pass. ESR spectra were recorded while the glass sample was irradiated with the cw Nd:YLF laser. The wavelength of the Nd:YLF laser was 523 nm. For vanadium-doped Nb_2O_5–TeO_2–K_2O glasses, 0.14 g of powder was put into a silica tube and the ESR measurements were performed on it.

3. Results

The glass compositions for the V_2O_5-doped Nb_2O_5–TeO_2 system shown in table 1 differ from each other in concentration of V_2O_5. Figure 2 shows optical absorption spectra for these glasses. The wavelength at which absorption drastically increases is longer for tellurite glasses with larger contents of V_2O_5. The absorbance at the wavelength of the seeding beam (532 nm), which lies in the tail of the intense absorption, increases with increase in the amount of V_2O_5. The intense absorption is presumably attributable to the charge transfer in the V^{5+}–O^{2-} bond. The absorption due to V^{4+} or VO^{2+}, the presence of which was confirmed by means of ESR for $15Nb_2O_5 \cdot 85TeO_2$ glass doped with 1 mol% V_2O_5 as discussed below, should appear at 420, 760–860, and about 1000 nm [18]. The absorption lines ascribed to V^{4+} are not observed in figure 2 because the concentration of V^{4+} is so small that the absorption due to V^{4+} is hindered by the intense absorption in the short-wavelength region.

Unless optical poling was carried out, SHG was not observed in the present Nb_2O_5–TeO_2 glasses. Figure 3 depicts the results of SHG measurements for optically poled vanadium-doped $15Nb_2O_5 \cdot 85TeO_2$ glasses. In this figure we show the time dependence of the second-harmonic intensity relative to that of α-quartz after ceasing of the optical poling. All the glasses shown in figure 3 exhibit decay. At a period shorter than about 150 s after ceasing of the optical poling, the second-harmonic intensity increases with increase in the V_2O_5 content. In other words, the second-order nonlinearity induced by the laser irradiation is larger in the glass with
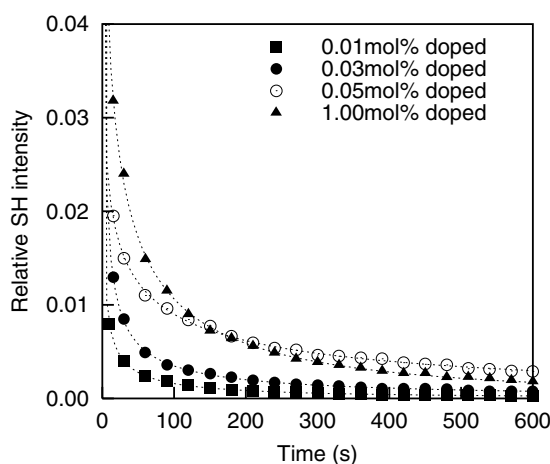
Figure 3. The time dependence of the second-harmonic intensity relative to that of α-quartz, i.e., the decay of the second-order nonlinearity, for optically poled $15Nb_2O_5 \cdot 85TeO_2$ glasses doped with 0.01, 0.03, 0.05, and 1 mol% V_2O_5.
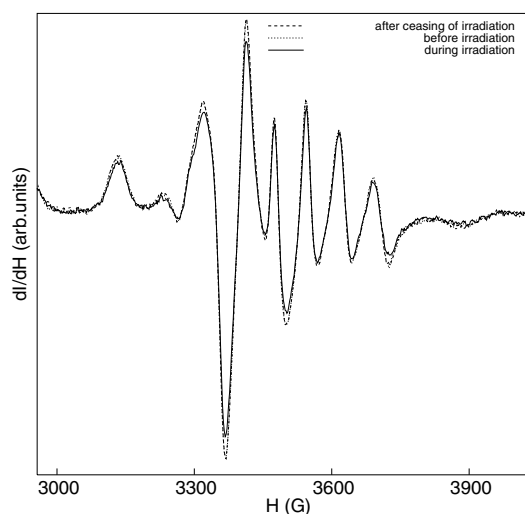

Figure 4. ESR spectra of $15Nb_2O_5 \cdot 85TeO_2$ glass doped with 1 mol% V_2O_5. The signal is attributable to V^{4+} or VO^{2+}. The ESR spectra before and during irradiation with a Nd:YLF laser whose wavelength is 523 nm are shown. The spectrum measured 30 min after ceasing of laser irradiation is also shown.

the larger content of V_2O_5. However, after a period longer than about 200 s after ceasing of poling, the second-harmonic intensity for 1 mol% vanadium-doped glass becomes less than that for 0.05 mol% vanadium-doped glass. That is, the decay rate is more rapid for 1 mol% vanadium-doped glass than for 0.05 mol% vanadium-doped glass.

In order to clarify the SHG mechanism for these glasses, it is very important to understand the state of vanadium ions in the glasses. Therefore, ESR spectroscopy was carried out for the glass doped with 1 mol% V_2O_5. Figure 4 shows the results of ESR spectroscopy. For as-prepared glass, a complicated signal ascribed to VO^{2+}, namely the tetravalent state of
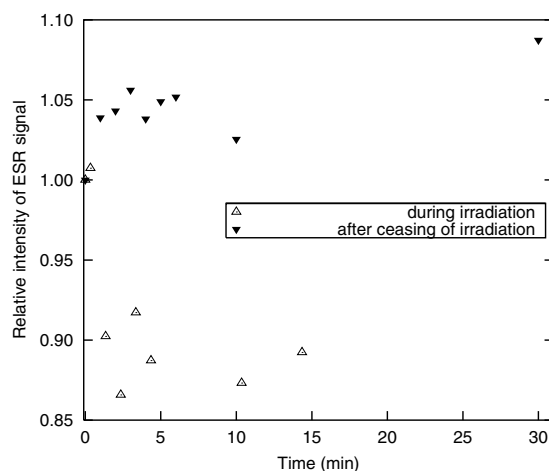
Figure 5. The dependence of the relative intensity of the ESR signal due to V^{4+} or VO^{2+} in $15Nb_2O_5 \cdot 85TeO_2$ glass doped with 1 mol% V_2O_5 on time of Nd:YLF laser irradiation (open triangles) and on time after ceasing of the Nd:YLF laser irradiation (closed triangles).

vanadium, was detected. We can conclude from this measurement that in the as-prepared V_2O_5-doped tellurite glasses, each vanadium ion takes either the tetravalent or pentavalent state; the pentavalent vanadium ions which have no unpaired electrons cannot be detected by means of ESR. In view of this result, ESR spectroscopy was performed for the glass irradiated with a SH wave of a Nd:YLF laser at a wavelength of 523 nm. As shown in figure 2, the glasses exhibit a little absorption at 523 nm. Irradiation with a Nd:YLF laser is expected to give rise to the same situation as optical poling. Hence, from the ESR measurements under irradiation with a Nd:YLF laser at 523 nm, we can evaluate the change of electronic states taking place during the optical poling. The ESR data before and after irradiation are shown in figure 4. A decrease in peak height of the signal assigned to the tetravalent state is confirmed, while no new peak appears upon laser irradiation. The variation of the relative intensity of the ESR signal due to VO^{2+} with time of laser irradiation is shown in figure 5 (open triangles). It is found that the relative intensity decreases with increase in time, and is apt to be saturated after laser irradiation for about 3–5 min. Figure 5 also shows the variation of the relative intensity of the ESR signal with time after ceasing of the laser irradiation (closed triangles). The intensity of the ESR signal due to VO^{2+} increases with increase in time.

Optical absorption spectroscopy and laser-induced SHG measurements were also performed for V_2O_5-doped Nb_2O_5–TeO_2–K_2O glasses with varied K_2O contents in order to examine the relationship between optically encoded second-harmonic intensity and absorbance at the wavelength of the SH wave used for optical poling. In the glass compositions shown in table 1, the molar ratio of TeO_2 to Nb_2O_5 was fixed. Optical absorption spectra of these glasses are shown in figure 6. It is found that the intense absorption shifts to a shorter-wavelength region as the content of K_2O is increased. In other words, the transmittance at 532 nm monotonically increases with increasing K_2O content. On the other hand, in figure 7 we show the variation of the second-harmonic intensity obtained 30 s after ceasing of optical poling with K_2O content in the V_2O_5-doped Nb_2O_5–TeO_2–K_2O glasses. The second-harmonic intensity is apt to increase with increase in K_2O content below 5 mol% of K_2O. For glasses with K_2O content larger than 5 mol%, the second-harmonic intensity decreases with increase in K_2O content. A similar behaviour is expected for the relationship between the second-harmonic intensity and the transmittance at 532 nm for the present glasses, as revealed in figures 6 and 7.
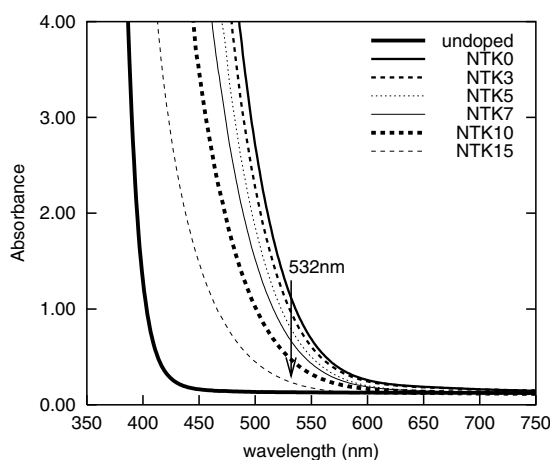
Figure 6. Optical absorption spectra for V_2O_5-doped Nb_2O_5–TeO_2–K_2O glasses with varied K_2O contents. The concentration of V_2O_5 is 0.5 mol%. The glass compositions are shown in table 1. The molar ratio of TeO_2 to Nb_2O_5 is fixed. The arrow indicates the wavelength of 532 nm.
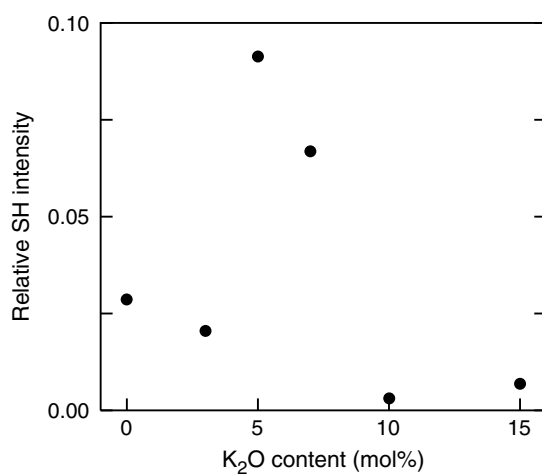

Figure 7. The K_2O content dependence of the second-harmonic intensity relative to that of α-quartz obtained at 30 s after ceasing of the optical poling on the K_2O content for the V_2O_5-doped Nb_2O_5–TeO_2–K_2O glasses.

4. Discussion

The present ternary Nb_2O_5–TeO_2–K_2O as well as binary Nb_2O_5–TeO_2 glasses doped with V_2O_5 clearly exhibit SHG after optical poling with two laser beams at 1064 and 532 nm. As shown in figure 3, the second-harmonic intensity for vanadium-doped $15Nb_2O_5 \cdot 85TeO_2$ glasses just after ceasing of the optical poling is about one hundredth of the second-harmonic intensity for α-quartz 1 mm thick. The second-harmonic intensity of the present vanadium-doped tellurite glasses is larger by about two orders of magnitude than those for $15Nb_2O_5 \cdot 85TeO_2$ glass without vanadium reported previously [17]. This result clearly indicates that vanadium plays an important role in the laser-induced SHG in the present tellurite glasses.

As shown in figure 5, the ESR measurements under Nd:YLF laser irradiation indicate that the number of V^{4+} or VO^{2+} present in the as-prepared glass decreased upon irradiation with light at 523 nm. This means that V^{4+} or VO^{2+} ions in the glass are converted into V^{5+} ions by irradiation with a Nd:YLF laser at 523 nm. In other words, an electron is released from the V^{4+} ion as a result of excitation by 523 nm light. The electron is thought to be trapped at certain levels. The positive V^{5+} ion, i.e., a positive hole trapped at a V^{4+} site, and the trapped electron can form an electric dipole or an internal dc electric field. The periodic arrangement of electric dipoles or periodic alternation of a dc electric field can produce a noncentrosymmetric structure leading to SHG. The increase in the number of V^{4+} ions with time after ceasing of optical poling shown in figure 5 reflects the decay of laser-induced second-harmonic nonlinearity depicted in figure 3, although the conditions for SHG and ESR measurements are not the same as each other; the decay of the second-harmonic intensity was measured while the glass was continuously irradiated with a laser, whereas the variation of the intensity of the ESR signal due to V^{4+} or VO^{2+} was obtained after the irradiation was ceased. Nonetheless, it is clear that the increase in the number of V^{4+} ions is closely related to the decay of the second-harmonic intensity for the vanadium-doped $15Nb_2O_5 \cdot 85TeO_2$ glasses.

The importance of absorption of light at 523–532 nm for optically encoded SHG is apparent in figures 6 and 7. As readily seen in these figures, the second-harmonic intensity is maximum when the transmittance is 15% or so, and is smaller in both regions of transmittance higher and lower than about 15%. The increase in second-harmonic intensity with decrease in transmittance at 532 nm in the range of higher transmittance indicates that absorption at 532 nm is required for the occurrence of SHG. This supports the mechanism of SHG, i.e., photo-oxidation reaction of V^{4+} induced by irradiation with a laser at 523 nm, which was deduced from ESR measurements. On the other hand, the second-harmonic intensity is low when the transmittance is lower than 10% or so. It is thought that this phenomenon is attributable to re-absorption of the second-harmonic wave at 532 nm generated from the glass. In addition, for the interpretation of figure 7, the compositional variation of the fraction of V^{4+} ions formed in glasses during the melting should be taken into account. In general, multivalent cations such as transition metal ions are apt to take oxidized states when the basicity of the glass increases. For the present tellurite glasses, addition of K_2O increases the basicity of the glass. Hence, the concentration of V^{4+} at oxidation–reduction equilibrium between V^{5+} and V^{4+} ions is expected to decrease as the content of K_2O is increased. We carried out ESR measurements on as-prepared glasses in the Nb_2O_5–TeO_2–K_2O system doped with 0.5 mol% V_2O_5. The ESR signals are shown in figure 8. It is clear that the concentration of V^{4+} decreases monotonically as the content of K_2O is increased. This is because the increase in K_2O content leads to an increase in basicity, i.e., the electron density on oxide ions in the glass, resulting in a situation where the oxidized state is more stable than the reduced state—V^{5+} is more stable than V^{4+} in the present case. Hence, in the glasses with large contents of K_2O, the number of V^{4+} ions, which are thought to be an origin for optically encoded SHG, is small. In other words, the small second-harmonic intensity observed for glasses with larger K_2O content is partly ascribable to the small concentration of V^{4+} ions.

In order to clarify the mechanism of laser-induced SHG in the present tellurite glasses doped with vanadium in more detail, we measured the variation of the concentration of V^{4+} with the power of the Nd:YLF laser. In figure 9 the change of relative intensity of the ESR signal due to V^{4+} or VO^{2+} caused by laser irradiation is plotted as a function of the laser power. The glass composition is $15Nb_2O_5 \cdot 85TeO_2$ doped with 1 mol% V_2O_5. In this figure, closed circles denote the experimental data, and the dotted curve is a calculated one drawn by means of the least-squares method. The curve is represented by

$$\Delta I/I \propto P_\omega^{2.0}, \tag{2}$$

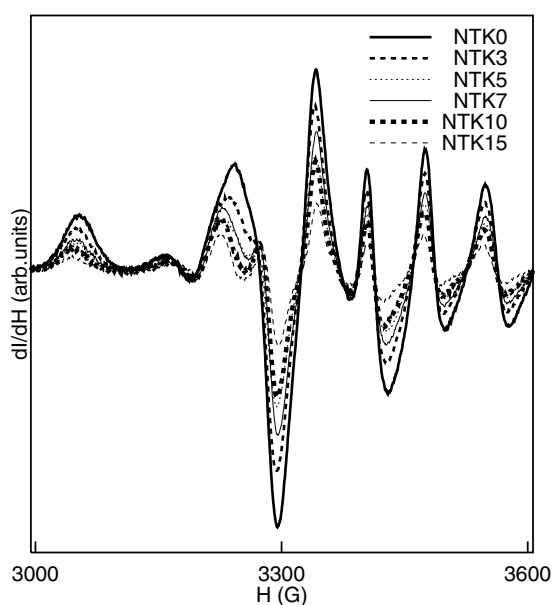**Figure 8.** ESR spectra of V^{4+} or VO^{2+} in Nb_2O_5–TeO_2–K_2O glasses doped with 0.5 mol% V_2O_5.
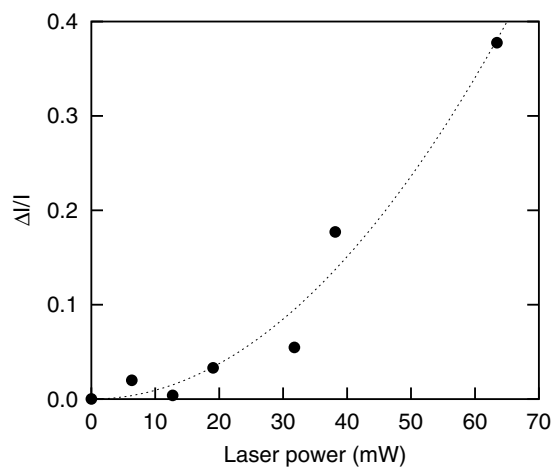

Figure 9. The change of relative intensity of the ESR signal due to V^{4+} or VO^{2+} caused by Nd:YLF laser irradiation as a function of laser power for $15Nb_2O_5 \cdot 85TeO_2$ glass doped with 1 mol% V_2O_5. Closed circles denote the experimental data. The dotted curve is a calculated one drawn by means of the least-squares method. The curve is described by the relation $\Delta I/I \propto P_\omega^{2.0}$, where $\Delta I/I$ is the relative change of intensity of the ESR signal and P_ω is the laser power.

where $\Delta I/I$ is the relative change of intensity of the ESR signal and P_ω is the laser power. This relation indicates that the number of V^{4+} ions changed into V^{5+} ions is almost proportional to the square of the laser power, suggesting that a two-step photon process is predominant in the conversion of V^{4+} into V^{5+}. On the basis of this result, we propose a possible model to explain the mechanism for photo-oxidation of V^{4+} and hence the formation of electric dipoles
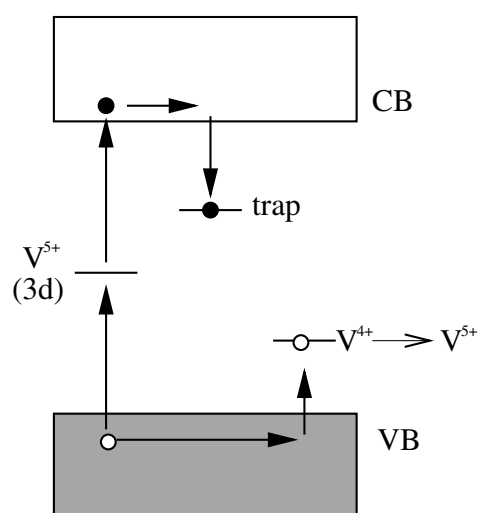
Figure 10. A schematic illustration for the mechanism of photo-induced conversion of V^{4+} into V^{5+} and formation of electric dipoles or an internal electric field leading to optically encoded SHG.

or an internal electric field leading to SHG. A schematic illustration of the mechanism is given in figure 10. When the glass is irradiated with a laser at 532 nm, an electron is transferred from the valence band presumably composed of 2p orbitals of oxide ions to vacant 3d orbitals of V^{5+}, and then it is further excited to the conduction band. Two photons are utilized in this process. The electron excited to the conduction band is trapped at a certain site. On the other hand, the positive hole formed in the valence band is trapped by V^{4+}. It is thought that the electron and positive hole lead to a spatial periodic variation of the electric dipoles or dc electric field whose periodicity is relevant to the wavelength of incident light, i.e., 1064 and 532 nm as suggested for laser-induced SHG in GeO_2-containing silica glass fibre [19, 20].

5. Conclusions

Optical poling leads to SHG in V_2O_5-doped tellurite glasses of the Nb_2O_5–TeO_2 and Nb_2O_5–TeO_2–K_2O systems. The second-harmonic intensity for the V_2O_5-doped Nb_2O_5–TeO_2 glasses is larger by two orders of magnitude than that of Nb_2O_5–TeO_2 glass without V_2O_5. In addition, for the Nb_2O_5–TeO_2 glasses doped with varied contents of V_2O_5, the second-harmonic intensity is increased as the content of V_2O_5 is increased. Thus, we revealed that the incorporation of vanadium ions effectively enhances the SHG in the present tellurite glasses. We consider that the optically encoded SHG is attributable to a periodic arrangement of electrons released from V^{4+} ions and positive holes trapped at V^{4+}-ion sites, both of which are induced during the optical poling. It is thought that the oxidation of V^{4+} into V^{5+} is caused by a two-step photon process at 532 nm.

Acknowledgment

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