Second Harmonic Generation from Electrically Poled PbO–SiO₂ Glasses

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電氣的にポーリングした PbO–SiO₂ ガラスからの第 2 高調波発生

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Clear second harmonic generation (SHG) was observed from $x\text{PbO} \cdot (100-x)\text{SiO}_2$ glasses after electrical poling. PbO can be considered to be responsible for the SHG center since no SHG was detected from electrically poled PbO-free SiO₂ glass. SHG was seen from the glasses poled above 100°C, and the intensity increased as the poling temperature increased. The minimum dc voltage necessary for SHG was 1 kV. SHG intensity increased first and then decreased with the increase of PbO content, showing a maximum at 34.8 mol% PbO. This dependence of SHG seems to relate the microstructure associated with Pb²⁺, probably Si–O–Pb²⁺ units.

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1. Introduction

It had been believed that SHG could not be found from homogeneous glasses since SHG could not be theoretically seen in optically isotropic materials until Sasaki and Ohmori¹⁾ and Osterberg and Margulis²⁾ reported SHG from Ge-doped SiO₂ glass fibers. Further studies on the SHG from fibers have revealed that the Ge E' center is closely related to SHG intensity.^{3,4)} On the other hand, Myers et al.⁵⁾ reported that SHG was also detectable from electrically polarized SiO₂ glasses. However, no oscillation was seen in the Maker-fringe pattern in Ref. 5), and thus the poled layer seemed to be limited at the surface of the glasses. They suggested the SHG might be attributed to the migration of the impurity Na⁺ ions. Similarly, Okada et al.⁶⁾ reported the SHG which has remarkable aging effect from deposited and corona-poled Corning 7059 glass film. They explained that the SHG was caused by the interface polarization. Previously, our group found SHG from SiO₂ glasses prepared by various techniques and with various OH concentrations after poling at over 150°C.⁷⁾ SHG intensity was increased as OH concentration was increased. Thereafter, SHG was observed from various kinds of glasses such as TiO₂ containing SiO₂ glasses,^{8,9)} TeO₂-based glasses,^{10–12)} γ-ray irradiated glasses,¹³⁾ electron beam irradiated glasses¹⁴⁾ and surface treated glasses with H₂O vapor.¹⁵⁾ From these results, it can be said that there are several ions possibly to form SHG centers. Among the recent reports on SHG glass, Kazansky et al.¹⁴⁾ noticed SHG from a commercial lead silicate glass. However, it cannot be easily considered that SHG is due to PbO since the commercial glass contains many kinds of constituents for different purposes. Therefore, present paper deals with high PbO containing binary silicate glasses to investigate the role of PbO to SHG and reports the dependence of SHG intensity on the composition and the poling condition.

2. Experimental procedure

Commercially available, analytical grade PbO (Nacalai Tesque) and optical grade SiO₂ were used as raw materials. These were weighed to $x\text{PbO} \cdot (100-x)\text{SiO}_2$ ($x=30, 40, 50, 60$ mol%) and mixed well. Then, each 30 g mixed powder was put into an alumina crucible and melted in an electric furnace in air at 900–1400°C for 1h with an alumina

cap. Then, the melts were poured onto an stainless steel plate and quenched by sandwiching with another plate. Subsequently, the quenched bodies were annealed at 300–570°C in an electric furnace for 1h. For the SHG measurement, both sides of the bodies were parallelly polished to optical grade, and thickness of the glasses was nearly 1.0 or 0.5 mm. The Au electrodes were deposited onto the both sides of the bodies. The electrode was rectangular of nearly 1 cm × 1 cm. The electrical poling was carried out from room temperature to 300°C, by applying dc 0–3 kV for 2 or 6h in air. Then, the samples were cooled down to room temperature with applying the dc voltage. After poling, the electrodes were taken away by mechanical polishing.

The intensity of second harmonic generation was measured by Maker-fringe technique. The experimental setup can be found elsewhere.^{7,8)} Infrared spectra were measured to determine the OH concentration in the glasses. In order to determine the composition of glasses, we measured X-ray photoelectron spectroscopy (XPS) spectra using Shimadzu ESCA 750 with X-ray source of Mg Kα line.

3. Results and discussion

It is necessary to explore the real content of PbO in the quenched glasses since PbO is more volatile than the other components. In the present work, the PbO content was estimated by comparing from the XPS peak areas of Pb and Si. In the present system, the melts are corrosive because of the high content of PbO and thus the Al₂O₃ contamination might be taken place. But no Al contamination was found from XPS spectra. The resultant composition for nominal 30PbO·70SiO₂, 40PbO·60SiO₂, 50PbO·50SiO₂ and 60PbO·40SiO₂ (mol%) glasses were 25.4PbO·74.6SiO₂, 34.8PbO·65.2SiO₂, 45.5PbO·54.5SiO₂ and 54.3PbO·45.7SiO₂ (mol%) glasses, respectively. Hereafter, the composition will be expressed as the resultant composition. The experimental error in composition was within 5 %.

Figure 1 shows a typical Maker-fringe pattern of 34.8PbO·65.2SiO₂ mol% with thickness of 0.5 mm, which was poled with 3 kV at 300°C for 6h. The polishing with hand frequently yield asymmetrical pattern between the positive and negative rotation angle areas caused by the lack of perfect surface smoothness and parallelism. The

Fig. 1. Typical Maker-fringe pattern from electrically polarized PbO-SiO₂ glasses (34.8 mol%PbO·65.2 mol%SiO₂ glass). Poling was carried out at 300°C for 6h with 3 kV.

asymmetric pattern in Fig. 1 is considered to be a typical one. The maximum of the SHG exists between 50–60°, indicating that the dipoles formed by poling are orientated parallel to the incident beam direction.

The interference of the SHG causes oscillation pattern when the poled layer is thicker than the coherent length, otherwise only a broad pattern should be observed.¹⁶⁾ Since one can see the oscillation in Fig. 1, the thickness of the poled layer should be thicker than coherent length. Estimation of the thickness of the poled layer (L) for this pattern was carried out with the following equations.

$$L = \lambda / 2\Delta m [\Delta n(\theta_i) - \Delta n(\theta_j)] \quad (1)$$

$$\Delta m = j - i$$

$$\Delta n(\theta) = n_{2\omega} \cos \theta' - n_{\omega} \cos \theta' = (n_{2\omega}^2 - \sin^2 \theta)^{1/2} - (n_{\omega}^2 - \sin^2 \theta)^{1/2} \quad (2)$$

where i and j represent the fringe numbers, n_{ω} and $n_{2\omega}$ represent the refractive indices at wavelengths of ω and 2ω , respectively, θ_i and θ_j represent the incident angles of the i th and j th fringe, respectively, and θ' is derived from Fresnel's rule, $\sin \theta = \sin \theta' / n$. We calculated the thickness of poled layer for the fringe pattern in Fig. 1 to be approximately 450 μm , corresponding to the sample thickness (0.5 mm). Therefore, the glass is poled over the entire body in direction of thickness. Furthermore, SHG was stably observed from the glasses even after being kept in the modest atmosphere for at least a couple of months. Thus, it can be said that this SHG is not caused from unstable surface polarization but oriented dipoles expanded into bulk sample.

As previously indicated,⁷⁾ OH in the glasses could be a SHG center, and SHG is observable in the glasses containing OH over 300 ppm. The concentration of OH in the present glasses was below 100 ppm. Thus, the SHG observed in the present glass cannot be attributed to OH. Myers et al. suggested that the impurity ions such as alkali ions possibly contribute SHG for their fused SiO₂ glasses. For the present glasses and the present procedure of poling and measurements, no SHG signal is detectable for pure SiO₂ glass and for high alkali-content SiO₂ glasses such as 7.5 Cs₂O·7.5K₂O·85SiO₂ glass.⁸⁾ From these experimental results, the impurity ions such as alkali ions is said not to be SHG centers only by themselves. Therefore, SHG centers of the present glasses should be related to other factors which will be discussed below.

Figure 2 depicts the dependence of SHG intensity on the poling temperature with constant poling dc voltage (3 kV) and time (2h) for 45.5PbO·54.5SiO₂ glass. SHG starts to be detected at 100°C and the intensity increases with increasing poling temperature, and seems to be saturated above 200°C. The poling above 300°C was impossible because of low glass transition temperature.¹⁷⁾ The

Fig. 2. SHG intensity as a function of poling temperature (by 3 kV for 2h).

dependence of SHG intensity on the poling voltage with constant temperature (300°C) and time (2h) is shown in Fig. 3. SHG is observable above 1 kV and increases as the voltage increases in the examined voltage range.

Figure 4 shows the influence of composition on the SHG intensity for PbO-SiO₂ system. One can notice the intensity maximum at 34.8 mol% PbO, and no SHG can be detected at 54.3 mol% PbO.

Eventually, SHG was observed from PbO-containing SiO₂ glasses, but not from PbO-free silicate glasses such as SiO₂ and alkali silicate glasses. Also, SHG was not observed from unpoled glass. Therefore, it can be noted the addition of PbO and poling procedure resulted in SHG.

As mentioned above, the oscillation in Maker-fringe pat-

Fig. 3. SHG intensity as a function of poling voltage (at 300°C for 2h).

Fig. 4. SHG intensity as a function of PbO content (at 300°C by 3 kV for 2h).

tern is clearly observed, indicating that poled layer is thicker than the coherent length and entire glass body is successfully poled. Similarly, in OH containing SiO_2 glasses, it was found that the poled layer has been spread out almost entire sample bodies.⁷⁾ With respect to anions, the existence of OH^- was detected by infrared spectra, but OH^- concentration is insufficient to cause SHG as discussed above. Since no halide was used as a raw material and in whole processing, and since the melting and quenching was performed in air, halide contamination cannot be taken into account. Although PbO-SiO_2 melts are corrosive in particular high PbO content, no Al contamination could be found by XPS measurement. It can be interpreted the melting temperature was lowered in high PbO containing system from 1400°C to 900°C, and no SHG was observed from mixed alkali silicate glass melted in alumina crucible at 1550°C. The contribution of Al_2O_3 can be negligible. Therefore, in the present PbO-SiO_2 system, the presence of Pb^{2+} ions make it possible to observe SHG. Thus, the microstructure relating SHG centers should be intimately associated with Pb^{2+} .

In PbO-SiO_2 binary glasses, PbO not only has the function of network modifier, but can act as network former in high PbO-content. PbO begin to incorporated into glass network in the region of $\text{PbO} > 40 \text{ mol}\%$.¹⁸⁾ Thus, the two different roles of Pb^{2+} in the glass structure may cause the maximum in the relation between SHG intensity and PbO at near PbO 40 mol%.

According to NMR measurements,¹⁹⁾ the Pb^{207} chemical shift in PbO-SiO_2 glasses is seen to vary continuously with PbO content, and Pb is rather ionic below nearly 50 mol% PbO but rather covalent at high PbO content. Furthermore, PbO is most ionic at 35 and 40 mol% PbO. On the basis of infrared and Raman scattering spectra for a series of PbO-SiO_2 glasses, Worrell and Henshell mentioned the increase of Raman peaks at 1000 and 950 cm^{-1} for $\text{PbO} \cdot 2\text{SiO}_2$ glass resulting from the formation of polarizable Si-O^0 or Si-O^- in silica network broken by Pb^{2+} ions, and the Raman peaks became less polarizable by increasing of PbO content.²⁰⁾ They explained that more than two of the Si-O bonds of the silicon-oxygen tetrahedron results in a break of the continuity of the silica network, and then Pb^{2+} must participate in the formation of glass network, which causes the increase of the covalency of Pb^{2+} ions.²⁰⁾ The composition of each silicon-oxygen tetrahedron theoretically having one nonbridging oxygen corresponds to $\text{PbO} \cdot 2\text{SiO}_2$, to which the composition (35 mol% PbO) exhibiting most intense SHG is quite similar. Hosono et al. examined the electronic state of Pb^{2+} in the oxide glasses by using electron spin resonance (ESR).²¹⁾ They discussed the electronic state on the basis of Pb 6s character, and the maximum appeared at 40 $\text{PbO} \cdot 60\text{SiO}_2$ mol% glass for PbO-SiO_2 system. Their results imply that the dependence of the electronic state of Pb^{2+} valence level on PbO content changes near 40 mol% PbO.

From above various results in literature, it can be noticed that the SHG intensity increases as the increases of ionic Pb^{2+} ions content, in other words, the increase of $-\text{Si-O-Pb}^{2+}-\text{O-Si}-$ structure units, and also noticed that the intensity decreases as the increase of covalency of Pb^{2+} ions, in other words, as Pb^{2+} ions participate in glass network formation.

With respect to the dependence of poling temperature, 100°C was at least necessary for SHG. That for OH containing SiO_2 glasses was 150°C,⁷⁾ and that for TiO_2 -containing silicate glasses was 250°C.⁸⁾ In the former system, Si-O-H^+ is considered to play an important role on SHG. Since it is considered that the similarity in the minimum efficient poling temperature may be due to the similarity in the SHG

center, the SHG center in the present PbO-SiO_2 glass is assumed to be Si-O-Pb^{2+} like Si-O-H^+ in the OH containing SiO_2 glass. The minimum meaningful poling voltage was 1 kV (nearly 10 kV/cm), and no remarkable difference can be seen from the previous SHG glasses^{7),8)} on the voltage. Thus, it can be noted that once the SHG centers become movable, the electric power necessary for poling is similar for these three centers.

4. Conclusion

After the electrical poling treatment, SHG was seen from some PbO-SiO_2 glasses. Since clear fringe pattern was observed and calculated poled layer nearly corresponded to sample thickness, the orientation of dipole moments was expanded into entire sample body. But, no signal was obtained from PbO-free SiO_2 glass. Thus, SHG was attributable to PbO in those glasses. The SHG intensity from PbO-SiO_2 glasses depended on PbO content, and the most intense SHG was detected at 34.8 mol% PbO. With respect to the influence of the poling condition, the meaningful poling temperature was 100°C, being close to OH containing glasses but not to TiO_2 containing silicate glasses. The poling voltage needed was at least 1 kV (10 kV/cm).

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