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Second-order non-linearity in 70PbO-30B_2O_3 glasses by thermal/electric poling

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70PbO-30B_2O_3 glasses were prepared by traditional melting method and second-harmonic generation was observed in the glasses, induced by thermal/electric poling process. Second-harmonic generation intensity was also investigated by different poling time, voltage and temperature to optimize the poling parameters to improve $\chi^{(2)}$. The maximum $\chi^{(2)}$ in our study as great as 3.885 pm/V was obtained under the optimized poling condition with 40 minutes, 3.5 kV and 275 ^{0}C. The mechanism of second-harmonic generation in the PbO-B_2O_3 glasses was also discussed.

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1. Introduction

It is well known in the centrosymmetric materials or amorphous materials that second-order susceptibility should be zero and second-harmonic generation (SHG) is consequently forbidden. However, Sasaki *et al*. [1] and Osterberg *et al*. [2] have observed SHG in glass fibers and bulk glasses, which meant the centrosymmetry has been broken by poling treatment and induced SHG. And then more and more researchers try to find second-order nonlinear optical materials by different poling techniques and attempts are in progress to achieve waveguides for second-harmonic waves using amorphous materials especially low-cost glasses [3-7]. So it is urgent presently to search for some new SHG materials for waveguide applications in optical communications and integrated optics. Stolen *et al*. [8] proposed a mechanism based on electric-field-induced nonlinearities in which the field arises from a third-order optical rectification process. So it is interesting to prepare some amorphous materials with high third-order non-linearity to induce high $\chi^{(2)}$. Large third-order nonlinearity will be observed in PbO-B_2O_3 glasses due to the ultrafast distortion of the electron orbits surrounding the average positions of the nucleus of heavy atom of Pb [9,10], which will make PbO-B_2O_3 glasses show high $\chi^{(2)}$ with effective poling process [9,11]. In this paper**,** 70PbO-30B_2O_3 glasses were prepared and effective SHG was observed by thermal/electric poling process. Different poling time, voltages and temperatures were also performed to investigate the mechanism of SHG.

2. Experimental

The 70PbO-30B_2O_3 glasses were prepared using the traditional melt-quenching method. The melted glasses were annealed near the glass transition temperature (<20□) determined by differential thermal analyses (DTA) in muffle furnace. 10 ×10 ×1 mm^{3}glass plates were obtained from the bulk glasses and optically polished on both sides for thermal/electric poling process.

The Vis-NIR transmission spectra of samples were recorded at room temperature with an ultraviolet spectrophotometer (Shi-Madzu UV-1601) with the wavelength range 190-1200 nm. The as-prepared glass plates were physically contacted to copper electrodes with the same central axis in air, and then were applied with different poling temperatures, time and voltages. Every time, the voltage was removed till the temperature decreased to room temperature.

Table 1. Compositions, T_g and T_c of PbO-B_2O_3 glasses[10].

Samples	PbO (mol%)	B_2O_3 (mol%)	T_g□◎□	T_c □◎□
1#	30	70	454	400
2#	40	60	430	390
3#	50	50	400	345
4#	60	40	340	300
5#	70	30	310	265
6#	80	20	300	250

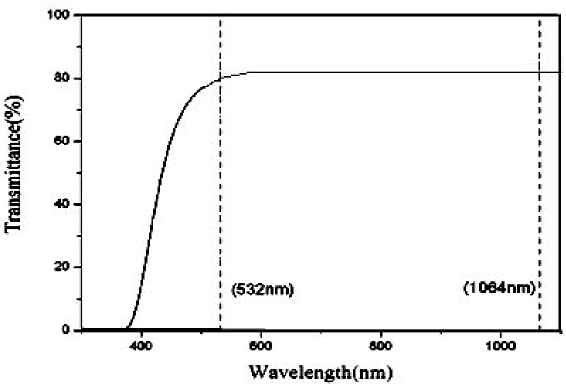

Fig. 1. Transmittance spectrum of 70PbO-30B_2O_3 glasses.

SHG measurements for 70PbO-30B_2O_3 glasses were performed with Maker Fringe [12] by using a pulsed Nd: yttrium-aluminum-garnet (YAG) laser with a pulse width of 10 ns. The fundamental wave with 1064 nm wavelength was used as an incident light. The output light from the glass plate went through a filter to divide the SH wave with 532 nm from the fundamental wave. The SH wave was detected with a photomultiplier and averaged by a boxcar integrator. Samples were placed on a rotating stage. The measurements were performed at consecutive angles of incidence from -80° to 80°. The reference sample was α-quartz (thinkness=0.782 mm) and its Maker Fringe pattern was shown in Fig.5(a). The thinkness of the nonlinear layer of glass samples was measured by etching method (5% HF solution) and it was about 14~20μm.

3. Results and discussion

The transmittance of glass as non-linear materials is essential for its potential application on all-optical optoelectronic devices like optical switching. The transmittance of amorphous 70PbO-30B_2O_3 glass as high as 80% is shown in Fig.1. The absorption edge of glass is less than 420 nm. In our present Maker Fringe measurements, the incident wavelength is 1064 nm and the output light from the glass plate went through a filter to divide the SH wave with 532 nm from the fundamental wave, so no absorption will occur during SHG measurements.

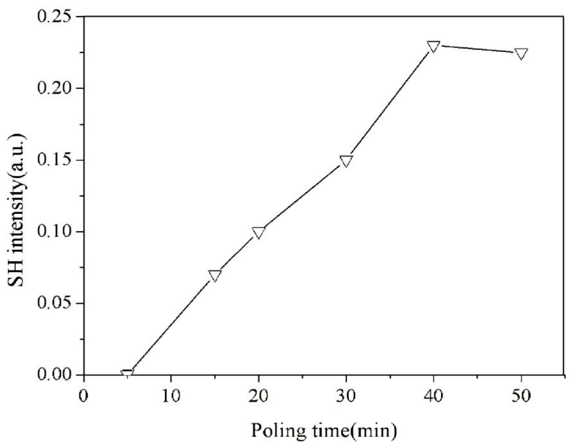

Fig. 2. The dependence of SH intensity on the poling time for 70PbO-30B_2O_3 glasses with 3kV and 300℃.

SHG was observed in 70PbO-30B_2O_3 with effective thermally/electrically poling process. We have studied the effect of different PbO content on SHG. It was indicated that SH increased with increasing PbO content, which meant PbO played an important role to induce SHG by thermal/electric poling in the glasses [13]. So we selected 70PbO-30B_2O_3 glasses to study its SHG in our present work. Normally the electric dipoles in glasses are restricted by the network configuration [14]. So there should be no second-order nonlinearity due to their effective centro-symmetry. But with effective thermal/electric application, the dipoles will move quickly, which help them to break their restriction and change the structure of glass to induce SHG in the glasses. As the existence of Pb, non-linear distortion of electron orbits in PbO-B_2O_3 glasses occurs easily to induce large second-order nonlinear effect with effective poling process in glasses [10, 13]. So large SHG in the 70PbO-30B_2O_3 glasses was observed by the effective thermal/electric poling process. Further SHG study of 70PbO-30B_2O_3 glasses with different thermal/electric poling voltages, time and temperatures were also performed to investigate the effects of thermal/electric poling parameters on SHG to make good understanding of second-order non-linearity in $70PbO\text{-}30B_2O_3$ glasses, which would also make thermal/electric poling mechanism clear to create great interest for practical applications and underlying physics about nonlinear optical glasses.

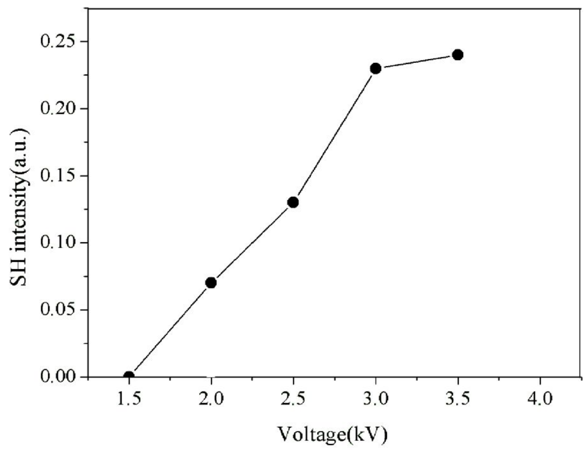

Fig. .3. The dependence of SH intensity on the poling voltage for $70PbO\text{-}30B_2O_3$ glasses with 300 ℃ and 40 minutes.

With 3kV and 300^0C, it was shown from Fig. 2 that SH intensity increased when the poling time increased. And at 40 minutes, SH intensity showed a maximum and saturated value, which meant that a saturation of the movement and alignment of dipoles occurred in the glasses during the thermal/electric poling process with this poling time. So the 40 minutes poling time value was the best treatment to induce SHG with 300 ^{0}C and 3.0 kV.

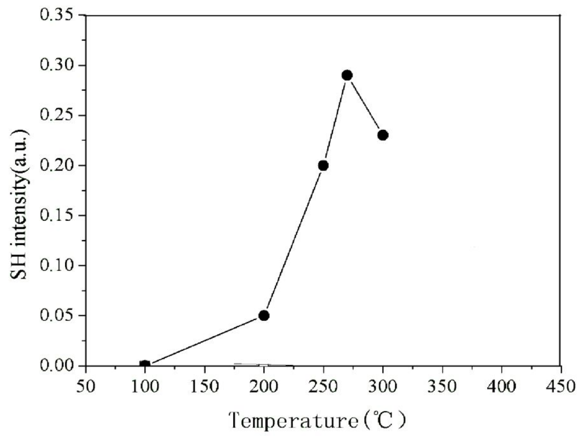

Fig. 4. The dependence of SH intensity on the poling temperature for $70PbO\text{-}30B_2O_3$ glasses with 3kV and 40 minutes.

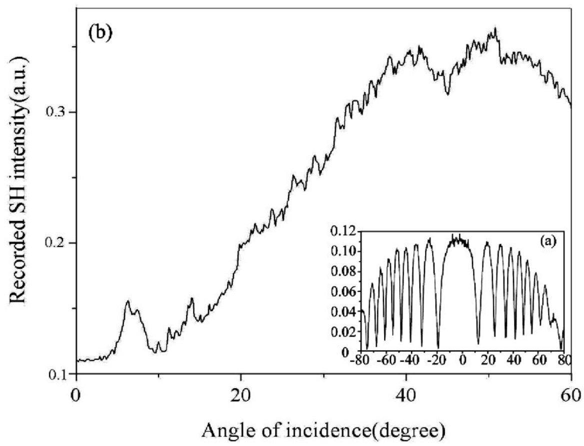

Fig. 5. (a) Maker Fringe pattern of standard SiO_2 crystal, (b) Maker Fringe pattern of $70PbO\text{-}30B_2O_3$ glasses with 40 minutes, 3.5 kV and 275℃ optimized poling condition.

The applied electric field provided the external driving force to align dipoles during the thermal/electric poling process. It was shown from Fig.3 that there was no SH signal when the applied voltage was smaller than 1.5 kV with 300 ^{0}C and 40 minutes. It was indicated that this poling voltage was not high enough to provide the required driving force to align dipoles although they gained enough energy to move quickly. When the poling voltage was higher than 1.5 kV, SHG was observed in the glasses. SH intensity increased with increasing poling voltage. But when the voltage was more than 3.5 kV, we could not do further experiments due to limitation of our thermal/electric poling set-up.

It was also seen from Fig.4 that SH intensity increased with the increasing of thermal/electric poling temperature in our experiments. Because high poling temperature accelerated the movability of dipoles and also weakened the restriction of glass network to them, which made dipoles align easily along the direction of the applied thermal/electric poling electric field. When the thermal/electric poling temperature was 275 ^{0}C, SH intensity showed a maximum and saturated value, which meant that there also existed a saturation of the movement and alignment of dipoles in the glasses during the thermal/electric poling process when temperature increased. So the 275 ^{0}C poling temperature value was the best heat treatment to induce SHG with 3.0 kV and 40 minutes.

It was indicated from Figs. 2, 3 and 4 that the effective thermal/electric poling process with 40 minutes, 3.5 kV and 275℃ poling condition met the need of optimized poling parameters to induce large SHG in glasses, which was performed and shown from Fig. 5 that effective SHG was observed from the Maker fringe measurements. The analysis of experimental SHG was carried out according to the Maker fringe theory [12]. Large SHG with $\chi^{(2)}$ as great as 3.885 pm/V was obtained from Fig. 5 with the optimized thermal/electric poling process at 3.5 kV, 275 ℃ for 40 minutes. The Maker Fringe pattern of standard SiO_2 crystal was shown in the Fig 5(a). Comparing with silica [7,15] and some chalcogenide glasses [3], it is larger and the reason of that is given in our investigation by Secondary Electron Emission Yield (SEEY) technique [15].

4. Conclusions

Second-harmonic generation was observed in the transparent 70PbO-30B_2O_3 glasses with effective thermal/electric poling process, which was related to the movement and alignment of the dipoles. Second-order optical nonlinearity $\chi^{(2)}$ as great as 3.885 pm/V was obtained by the optimized thermal/electric poling process with 3.5 kV, 275 □ and 40 minutes. 70PbO-30B_2O_3 glasses will show great potential applications on the glass-based optoelectronic devices like optical switching due to its easy fabrication of thermal/electric poling, comparatively large nonlinearity and high transmittance.

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