

Novel Thermally Stable Cross-Linked Nonlinear Optical Silica Films Prepared by a Sol–Gel Process

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To improve the orientational stability of the chromophore induced by an electric field in a second-order nonlinear optical polymer, we have synthesized a thermally stable and cross-linkable azo dye, 4-[(4''-aminophenyl)sulfonyl]-4'-[N,N-bis(2-hydroxyethyl)amino]azobenzene. The transparent films with silica as matrix and organic chromophore as cross-linking agent were then prepared by using a sol–gel process. The resulting films heated at 200 °C under a high-corona field exhibited the nonlinear optical coefficient $d_{33} = 32$ pm/V in Maker-fringe measurement. Long-term stability of second-harmonic coefficients in these films was observed even at 160 °C.

Introduction

Poled amorphous polymers with the incorporation of nonlinear optical chromophores have attracted a large number of researchers due to the polymers' easy processability for fabricating thin films for optical applications.^{1–3} However, because of the rotational freedom of the chromophore and relaxation of the main chain, second-order nonlinear optical properties are generally not very stable when the temperature approaches the glass transition temperature (T_g) of the matrix. Efforts to increase the thermal stability entail selecting high glass transition temperature matrixes (e.g., those with cross-linking),^{4,5} main-chain chromophores,⁶ or high glass transition polymers.⁷ From the current literature, it appears that polyimide and transparent films containing NLO chromophores prepared by a sol–gel process are the two most potential candidates which may retain largest temporal behaviors.^{8–13}

In our previous paper,¹⁴ it was shown that chromophores cross-linked to a silica glass matrix exhibit the highest poling orientation stability. We also concluded that a high sintering (poling) temperature can convert a wet gel into a dry gel with a more condensed structure, further confining the chromophore's rotational movement. To synthesize a chromophore with high decomposition temperature and more than three reactive sites for linkage is therefore necessary for obtaining a highly stable nonlinear optical silica film. Similar work has been conducted by Dalton et al.,^{15,16} they chose 4-(2-hydroxyethylsulfonyl)-4'-[N,N-bis(2-hydroxyethyl)amino]azobenzene as the reactive chromophore and obtained stable second-order optical nonlinearity at 100 °C.

In the present work, we have attempted to synthesize a highly thermally stable chromophore, which contains three reactive sites on both ends of the chromophore. Unlike other polymer systems previously described, this material has no flexible spacer between the sulfonyl group and the urethane linkage. The decomposition temperature of the silica film is therefore increased significantly. The temporal behaviors of the final poled silica films are also discussed.

Experimental Section

Preparation of Chromophore. 4-[(4''-Aminophenyl)sulfonyl]-4'-[N,N-bis(2-hydroxyethyl)amino]azoben-

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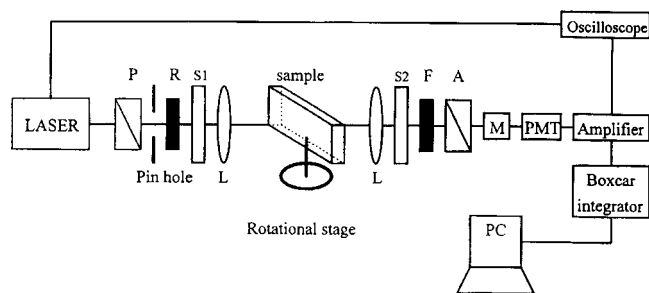


Figure 1. Diagram of the experimental setup: (P) polarizer; (R) half-wave retardation; (S1) harmonic separator for 1064 nm; (L) lens, focal length 150 mm; (S2) harmonic separator for 532 nm; (F) high-power filter; (A) analyzer; and (M) monochromator.

zene (APSHAB). The maleic anhydride (0.98 g, 10.0 mmol) was dissolved in 5 mL of dry acetone and then added dropwise to 4,4'-diaminodiphenylsulfone (2.48 g, 10.0 mmol) in 10 mL of dried acetone at 25 °C. After the mixture was stirred for 8 h, the milky white precipitate was collected and washed several times with cold acetone. The yield of amic acid (**1**) was 74%. Compound **1** (3.46 g, 10.0 mmol) was dissolved in 6 M sulfuric acid (12 mL) and diazotized with sodium nitrite (0.69 g in 5 mL of H₂O, 10.0 mmol) at 0–5 °C. The mixture was then added dropwise to bis(hydroxyethyl)aniline (1.81 g, 10.0 mmol) in acetic acid (10.0 mL) at 0–5 °C and mixed for 5 h. The reaction mixture was stirred overnight at room temperature. Aqueous NaOH (3 N) solution was then added to neutralize the mixture. The orange precipitate was collected and washed several times with water until the pH was ~7. The precipitate was dried in the oven at 100 °C, yielding **2**: 2.50 g; yield, 46%. Compound **2** (1.00 g) was added to a refluxed solution containing 6 N aqueous HCl (50 mL) and methanol (50 mL). The mixture was refluxed for 20 min. The mixture was filtered immediately while the temperature was still high. The 3 N NaOH aqueous solution was then added to neutralize the filtrate until the precipitation occurred. Finally, the methanol was removed on the Rotovap. The product was poured into iced water and filtered until the pH was ~7. Recrystallization from ethanol yielded APSHAB: 0.64 g; yield, 78%; mp 178 °C.

¹H NMR (DMSO-*d*₆): δ 7.94 (2H, d, *J* = 8.6 Hz), 7.85 (2H, d, *J* = 8.6 Hz), 7.77 (2H, d, *J* = 9.0 Hz), 7.57 (2H, d, *J* = 8.7 Hz), 6.87 (2H, d, *J* = 9.0 Hz), 6.63 (2H, d, *J* = 8.7 Hz), 6.20 (2H, s), 4.84 (2H, s), 3.60 (8H, s). UV-vis (acetone): λ_{max} = 450 nm. Molecular mass: calcd, 440.1518; found, 440.1519.

Preparation of Alkoxysilane Containing Chromophore (As-APSHAB). As-APSHAB was prepared by refluxing APSHAB for 48 h in THF solution containing 3-isocyanatopropyltriethoxysilane with a small amount of triethylamine as catalyst. The reaction was monitored while the characteristic IR absorption peak at 2270 cm⁻¹ for the isocyanate group was diminished. The product was then precipitated from *n*-hexane and dried under vacuum.

Measurements. Infrared spectra were recorded on a Perkin-Elmer 1600 spectrophotometer. UV-vis absorption spectra were measured by transmission on a Hitachi U-2000 spectrophotometer. ¹H NMR was conducted with a Bruker AC-F300 spectrometer with TMS as internal reference. Thermogravimetric analysis was performed with a Du Pont TGA-951 thermal analyzer at 10 °C min⁻¹ under N₂.

Second harmonic generation (SHG) measurements were performed using the Maker-fringe technique. A diagram of the experimental setup is shown in Figure 1. The light source was a Spectral Physics GCR-200 Q-switched Nd:YAG laser at a wavelength of 1.064 μm. The repetition rate was 10 Hz, and the pulse rate was 8–9 pulses ns⁻¹. The typical energy per pulse was <20 mJ. The transmitted beam was passed through colored glass filters and a monochromator to eliminate all traces of the fundamental light. The SHG signal was detected by a Hamamatsu R636 photomultiplier tube monitored by a Tektronix TDS 620A oscilloscope and processed by a Stanford

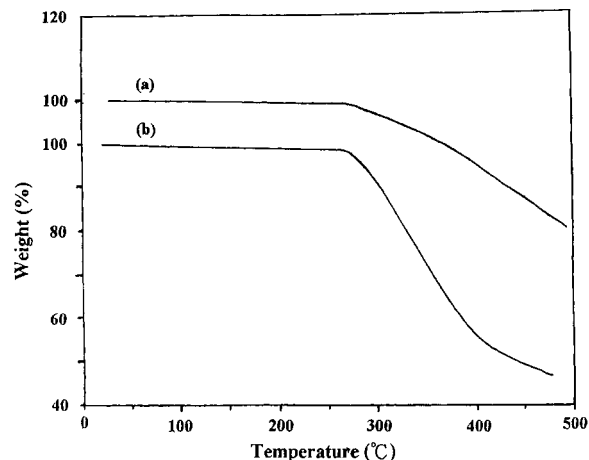


Figure 2. TGA traces for (a) As-APSHAB silica films and (b) APSHAB.

Research System SR-250 Boxcar integrator. The second-harmonic coefficients of the poled polymers and a Y-cut quartz sample were then calculated at the same time and compared. In this experiment, the S-S polarization geometry was used; the *d*₃₃ value of the polymer and the *d*₁₁ value of the quartz can be obtained from Maker-fringe patterns readily.

Results and Discussion

To improve the thermal properties of the chromophore, the design involves introducing a more rigid phenyl ring to the sulfonyl group in the chromophore main chain. Chemical structures of the starting materials and the reaction sequence are shown in Scheme 1. In accord with the literature,¹⁷ we used maleic anhydride to protect one side of the amine of 4,4'-diaminodiphenylsulfone. Maleic anhydride was added dropwise to a solution of an equimolar amount of diamine in dry acetone. Under these conditions, only monomaleamic acid derived from diamine was observed. The coupling reaction of the azo compound and the deprotection of maleamic acid followed conventional methods without any difficulty. TGA results showed that the chromophore possesses excellent thermal stability (decomposition temperature started at 270 °C), as shown in Figure 2. The UV-vis absorption peak (acetone as solvent) for APSHAB is at 450 nm.

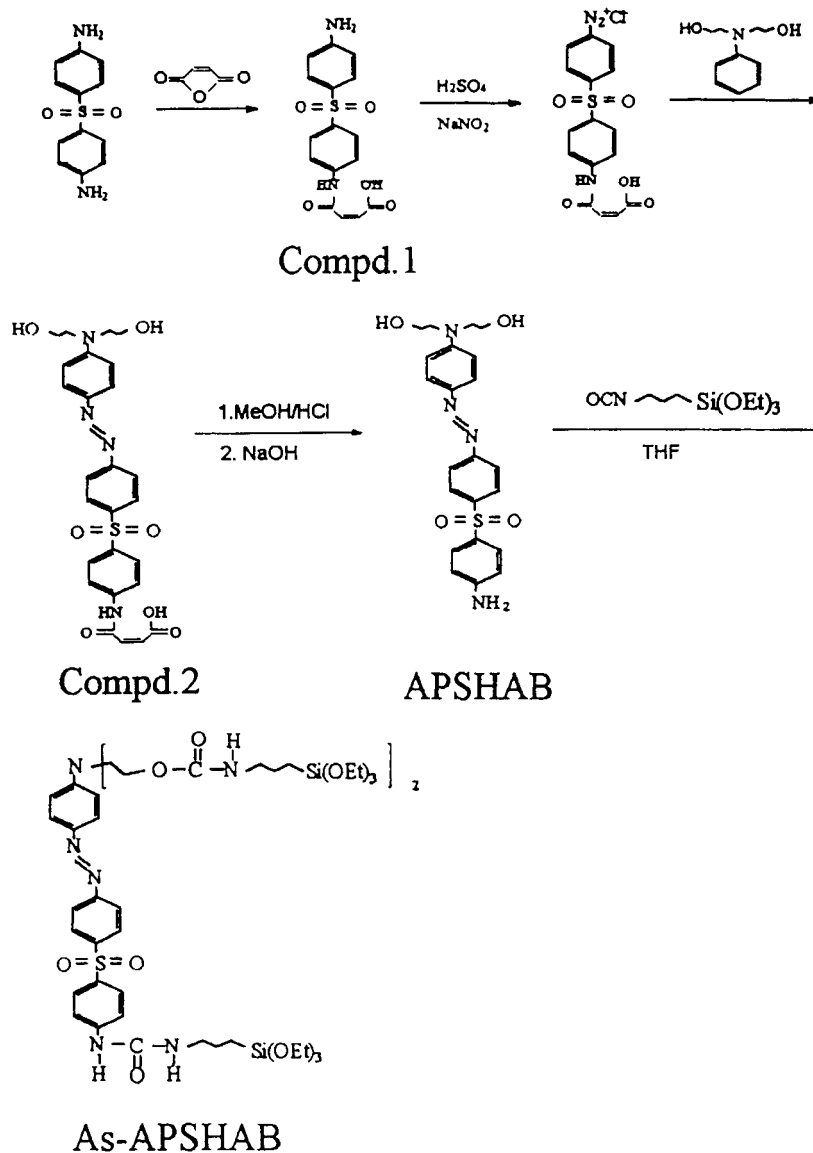
Scheme 1 also outlines the approach for synthesizing alkoxysilane containing chromophores. As-APSHAB was synthesized by coupling APSHAB with 3-isocyanatopropyltriethoxysilane. The isocyanate group is well-known to have a characteristic IR absorption peak at 2270 cm⁻¹.¹⁸ Therefore, it can be used as an indication of the degree of the reaction. As shown in Figure 3, the intensity diminished after the reaction proceeded at 64 °C for 2 days, thereby revealing the completeness of the reaction.

To prepare the coating solution, the alkoxysilane-terminated chromophore was mixed with tetraethoxysilane (TEOS) and water at a 1:10:25 molar ratio in various solvents. The solubility, polarity, and evaporation rate of the solvents will significantly affect the quality of the resulting coating films. By employing the com-

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Scheme 1. Synthesis of APSHAB and As-APSHAB



mon solvents (e.g., ethanol, THF, MEK, and NMP) used in the literature, after many attempts, we always obtained the coating films with phase separation or shrinkage. However, by using isopropyl alcohol/THF (60:40, v/v) as cosolvent, we were able to obtain uniform and transparent silica films. In the coating solution, a small amount of 0.25 N aqueous HCl was also added as a catalyst. The solution (10%, w/w, solid content) was stirred at room temperature for 1 day to increase the viscosity. The viscous solution was then filtered through a 0.5 μm Teflon filter before spin-casting onto transparent ITO (indium tin oxide) glass. The coated films were then vacuum-dried at room temperature for 4 h to remove the solvent. Figure 4 shows the structure of the organosilicate gel. The initial decomposition temperature of organosilicate film measured by TGA is 270 $^{\circ}\text{C}$, the same as the chromophore (Figure 2).

The disadvantage of designing a cross-linked type nonlinear optical polymer is the poor poling efficiency due to the fixation of the chromophore main structure to the polymer matrix via covalent bonds. To alleviate this problem, many studies based on chemical or photochemical cross-linking reactions after electrical

poling have been published.^{19–22} All such experiments show promising but not significant improvement in the stabilization of dipole alignment. To achieve optimum poling efficiency, conventional specimens are usually poled at a temperature close to the glass transition temperature (T_g) for a long period. However, no T_g could be observed in the organosilicate films, owing to the high T_g of silica matrix (>1000 $^{\circ}\text{C}$). As we mentioned in our previous paper,¹⁴ the polycondensation reaction is extremely slow at room temperature for the sol-gel silica film system. The coated solutions are composed of partly condensed organosilicates. This is why the chromophores of the cross-linking type organosilicate films are still able to align under the electric field. To increase the reaction rate, an elevated temperature is always chosen. Besides, a high sintering (poling) temperature converts wet gel into dry gel with

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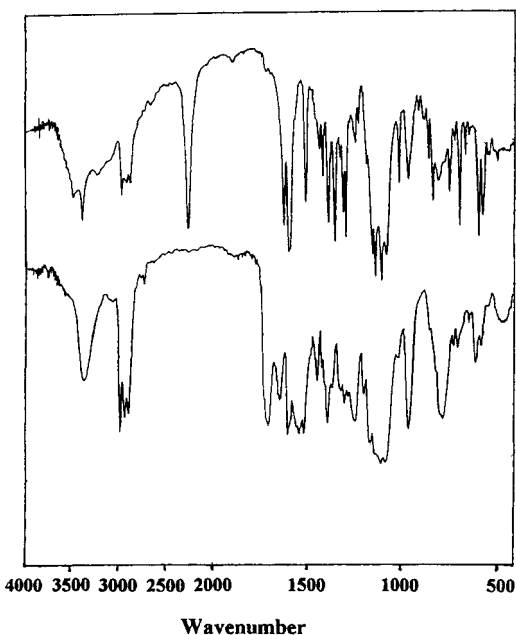


Figure 3. FT-IR spectra of pristine material and As-APSHAB.

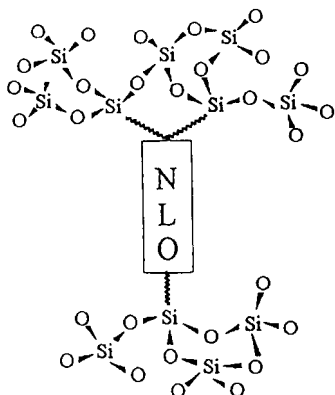


Figure 4. Structure of As-APSHAB silica films.

a more condensed structure, further confining the chromophore's rotational movement. It is therefore desired to raise the poling temperature as high as possible. However, the chromophore must not be decomposed under these conditions during the poling period. For this reason, the UV absorption of the organosilicate film at different temperatures was chosen to assess the long-term aging properties. Figure 5 shows the temporal behavior of the organosilicate films held at different temperatures for 16 h. According to Figure 5, the maximum temperature that can be tolerated is 200 °C, which is far below the decomposition temperature obtained by TGA. To prepare the poled As-APSHAB silica films, the specimens were heated by multistep schedules to 200 °C for 12 h and poled by using a corona discharge apparatus. The applied voltage on the corona wire was maintained at 5.5 kV with a current of 1.5 μ A. Cooling of the substrate was conducted under an applied field.

The UV-vis absorption spectra of the films before and after poling are shown in Figure 6. The pristine sample shows an absorption peak at 439 nm. After the poling process, a blue shift (432 nm) was observed due to induced dipole alignment.⁵ The order parameter is defined by $\Phi = 1 - (A_{\perp}/A_0)$, where A_{\perp} and A_0 are the

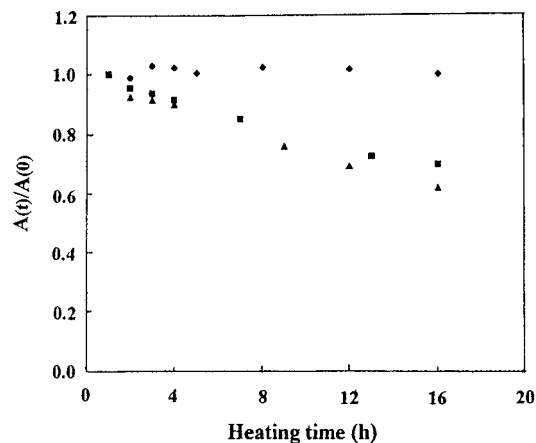


Figure 5. Relative UV absorbance of As-APSHAB silica films held at different temperatures: (◆) 200, (■) 210, and (▲) 220 °C.

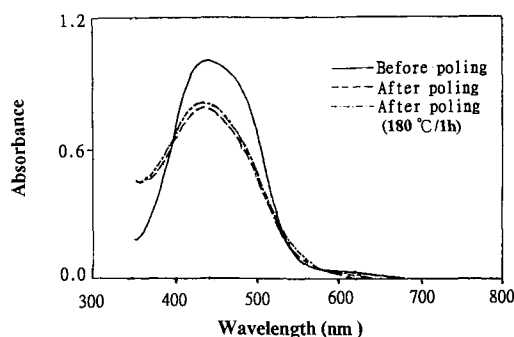


Figure 6. UV absorption spectra of As-APSHAB silica films before and after poling.

UV-vis absorbances of the poled and unpoled films, respectively.²³ Theoretically it can be used to estimate the degree of chromophore orientation. The moderate value of $\Phi = 0.24$ was observed due to partial cross-linking of the organosilicate coating solution before poling. The peak absorbance of the poled silica film only increased slightly after 1 h of aging at 180 °C. This result reveals that orientational stability of the chromophore in the cross-linked organosilicate film is excellent.

The second-order NLO properties of the silica films were characterized by second-harmonic generation (SHG) using the Maker-fringe technique. By comparison with the second-harmonic intensity generated by a standard quartz sample and the published value of $d_{11} = 0.5$ pm/V for quartz,²⁴ the d_{33} value of the As-APSHAB silica film is found to be 32 pm/V. The long-term stability of nonlinearity was studied both by dynamic stability measurements with a heating rate of 5 °C min⁻¹ and by measurements at various temperatures as a function of time. The SHG signals were recorded simultaneously in both tests. As seen in Figure 7, the nonlinearity starts to decay at around 130 °C. Up to 75% of the nonlinearity remained even at 160 °C, and 50% remained at 200 °C. For the long-term temporal behavior, it was found that the nonlinearity remains constant at 100 °C. The intensity started to decay while the

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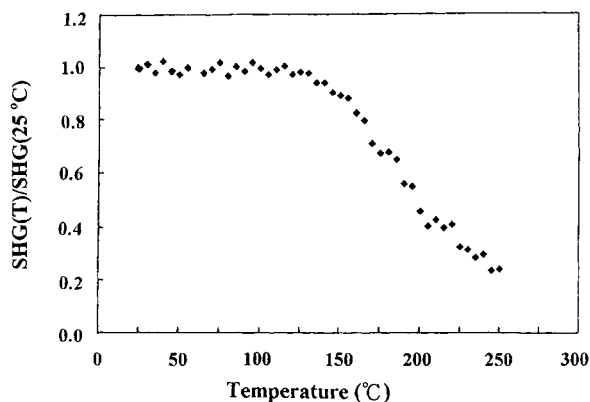


Figure 7. SHG signal of As-APSHAB silica films as a function of temperature.

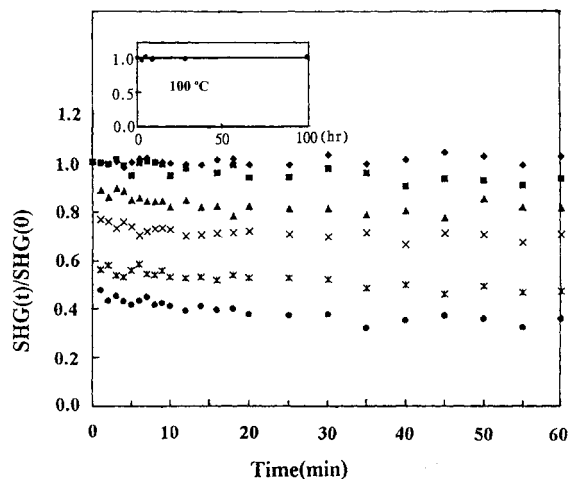


Figure 8. Thermal aging test of As-APSHAB silica films: (◆) 100, (■) 120, (▲) 140, (×) 160, (*) 180, and (●) 200 °C.

temperature was kept higher than 140 °C, as shown in Figure 8. This result is in agreement with the dynamic stability measurement. It is very interesting to point out that after the dramatic decrease of the nonlinearity in the first few minutes, the decay turns to level off even at higher temperatures. Although the other systems also showed a similar decay, they usually took several hours to reach equilibrium.^{25–27} The temporal stability of SHG efficiency at different temperatures (especially in the fast-decay region) reflects complex reorientational mechanisms, namely, decomposition of the chromophore, relaxation of the matrix, and relaxation of the chromophore due to thermodynamic equilibrium. Compared with the TGA results, it is believed that the chromophore does not decompose under the test conditions. Besides, the test temperature is far below the T_g of the silica glass; it is impossible to relax the matrix during such a short period of time (less than 3 min). The chromophores are anchored on both sides and highly cross-linked to the silica matrix; there is no way for the chromophores to rotate under any circumstances. The decay of the nonlinearity is therefore attributed to changes in the orientation of the chromophores. Con-

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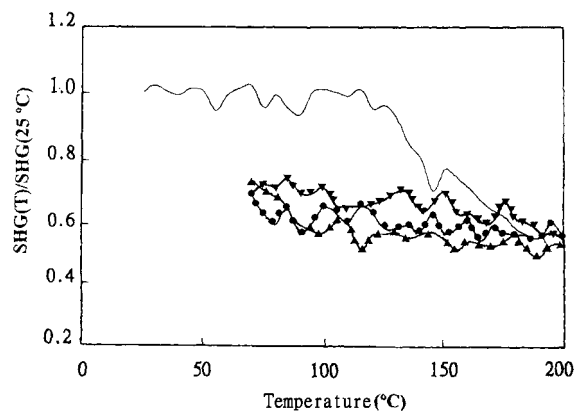


Figure 9. Temperature cycling of As-APSHAB silica film: (—) first run, heating; (●) first run, cooling; (▼) second run, heating; (▲) second run, cooling.

version of a wet gel to a dry gel consists of removing a large proportion of the remaining liquid phase (alcohol and water). To complete the reaction, it is suggested that the final sintering temperature may range from 600 to 1400 °C.²⁸ This temperature range is far above the decomposition temperature of the chromophore. In our system, a low poling temperature (200 °C) was chosen. Therefore, an incomplete polycondensation reaction of wet gel to dry gel is expected. Thus the silica matrix contains a broad cross-linking density distribution. At different temperatures, only the chromophores located on those less densely cross-linked sites have enough energy to vibrate. We hereby propose that the amplitude of the vibration, which is a function of the temperature, is the major contribution to the decay of the nonlinearity in our highly cross-linked sol-gel silica system. A temperature cycling (hysteresis) experiment was conducted to evaluate this concept. As seen in Figure 9, a partial recovery of nonlinearity (20%) upon cooling from high temperatures was observed in both temperature cycles. This result confirms our postulation. The SHG intensity gap between the first run (heating) data and the other data at 70 °C is probably due to the release of the internal stress that is irreversible.

In conclusion, we have prepared an ambient temperature processible silica film where NLO chromophores were covalently cross-linked into the silica matrix. A moderate poling efficiency was obtained under electric field. After the electric poling, the cross-linked material generated a very stable long-term second-harmonic signal even at 160 °C. Our preliminary results showed a partial recovery of nonlinearity (SHG intensity) upon cooling from high temperatures in a temperature cycling experiment, indicating that the vibrational amplitude of the chromophore might play the major role in the decay of nonlinearity. More detailed discussion on this result will be reported separately.

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