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Photosensitivity and second harmonic generation in chalcogenide arsenic sulfide poled glasses

Marc Dussauze,^{1,*} Xiaolin Zheng,^{2,3} Vincent Rodriguez,¹ Evelyne Fargin,⁴
Thierry Cardinal,⁴ and Frédéric Smektala²

¹Univ. Bordeaux, ISM, CNRS UMR 5255, F-33400 Talence, France

²Laboratoire Interdisciplinaire Carnot de Bourgogne, UMR 5209 CNRS-université de Bourgogne, 9 Av. Alain Savary, 21078 Dijon Cedex, France

³State Key Laboratory of Silicate Materials for Architectures, Wuhan University of Technology, Luoshi Road 122, Hongshan District, Wuhan 430070, China

⁴Univ. Bordeaux, ICMCB, CNRS UPR 9048, F-33600 Pessac, France

*m.dussauze@ism.u-bordeaux1.fr

Abstract: The present work investigates the photoinduced Second Harmonic Generation processes in thermally poled arsenic sulfide glasses. SHG Maker fringes patterns associated to SHG kinetic measurements about illumination and Raman spectroscopy have been conducted in order to bring new information which confirm the combined influence of charge carriers and mid-range glass structural modification on the poling and the photodarkening mechanisms.

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OCIS Codes: (160.2750) Glass and other amorphous materials; (190.4400) Nonlinear optics, materials; (160.4330) Nonlinear optical materials.

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1. Introduction

In the design of micro photonic devices, the tendency is to fabricate components, which could include light sources, but also detectors and all the active optical elements such as beam splitters, gratings, interferometers and finally to integrate all these optical functions on a unique material. Thus, for such an "integrated photonics" technology, the ideal material is expected to allow a three dimensional control of its linear as well as second and third order nonlinear optical responses at the micrometer scale [1,2]. To achieve these very promising objectives, chalcogenide glasses are potential candidates as they permit easy waveguide writing and they can exhibit large second and third order optical susceptibility [3–9].

Concerning second order optical properties of amorphous media, one of the most efficient processes used to break their centro-symmetry and achieve second-order optical capabilities is thermal poling. It consists in applying in contact an electric field at an elevated temperature and to cool down the material under the application of the field. Such a process was successfully applied on few chalcogenide glasses showing some of the most efficient second order optical responses in glassy materials [4–6]. However, it has been clearly demonstrated that the key point for poled chalcogenide materials concerns the stability in time of their second order optical response [10].

In the field of photoinduced effect, the photosensitivity of $\text{As}_x\text{S}_{(1-x)}$ glasses has been widely studied during the last decades [11–21]. The observed changes in optical, electrical, mechanical and rheological properties have been always linked to changes in atomic arrangements within the glass structure. However the photochemical and electrochemical processes are still not well understood in this class of amorphous materials.

These large bases of knowledge and state-of-the-art have encouraged us to study the possibility to modify linear and second order optical responses of arsenic sulfide glasses by combining thermal poling and irradiation processes. This paper reports on the influence of a poling treatment on both the second order optical response and photoinduced structural changes of arsenic sulfide glasses.

2. Experimental

Glass synthesis

Homogeneous glass samples were prepared by traditional melt-quenching method using high-purity (5N) elemental arsenic and sulfur and chemical-purity 2N sodium chloride. Three compositions of arsenic sulfide glasses were selected as the object of following studies, i.e. pure As_2S_3 without NaCl doping, As_2S_3 with 10 ppm NaCl and As_2S_3 with 100 ppm NaCl doping. The doping is in weight ppm and the glasses are hereinafter respectively labeled as AsSNa0, AsSNa10 and AsSNa100. For AsSNa0 samples, the details of the preparations were similar to our previous works [22]. However, for AsSNa10 and AsSNa100 samples, the melting temperature was increased to 850°C for NaCl doping and no distillations of sulfur were previously realized before melting, while for AsNa0 glass we have performed several sulfur distillations before the melting of the glass. Glass plates with 1mm thickness and 16mm diameter were obtained from the glass rods and optically polished for both sides. The variation of Na^+ ions concentration in the above three compositions has been confirmed by secondary ion mass spectroscopy (SIMS) analysis.

Poling

Poling treatments were done in air. The arsenic sulfide glasses were heated to a poling temperature of 100°C and polarized with a voltage of 5 kV applied for 30 min after the poling temperature was reached. Two different poling configurations have been used (i) n-doped silicon electrodes were used at both anode and cathode sides of the poled arsenic sulfide glass (ii) soda lime glass slides (100 μm thick) were introduced between the n-doped silicon electrodes and the arsenic sulfide glass to be polarized.

Raman

This experiment has been carried out using a micro-Raman spectrometer (HR800 Horiba/Jobin-Yvon) working in backscattering geometry using the 752 nm excitation line of a solid state laser with a typical spectral resolution of 3 cm^{-1} . The spectrophotometer included a holographic Notch filter for Rayleigh rejection, a microscope equipped with a 100 \times objective and a CCD air cooled detector.

SHG

Polarized SHG Maker fringe patterns were recorded using an OPO intra cavity laser operating at 1550 nm, at low irradiance. Depending on the experiments, a maximum energy of 200 μJ on the sample was used. The pulse width and the repetition rate of laser pulses were about 10 ns and 30 Hz, respectively. The fundamental intensity was monitored using a fiber with a large numerical aperture placed close to a mirror to collect the scattered fundamental light quantified by an InGaAs photodiode connected at the output of the fiber. Second harmonic generation (SHG) transmitted signals were detected by a photomultiplier and averaged over 50 pulses. SHG signals were recorded with p-p polarization configurations, i.e. p-polarized incident pump beam and p-polarized transmitted second harmonic beam. Two different measurements were carried out. First, θ -scans were recorded, i.e. the classical Maker fringes experiment where the SHG intensity is recorded in function of the angle of incidence θ between the laser beam and the normal to the sample surface. In this first experiment, a home-made laser beam shutter was synchronized with the SHG acquisition for each angle θ to minimize the irradiation of the sample. Second, SHG kinetic measurements were performed

under a continuous laser irradiation to determine the SHG stability as a function of the laser irradiation at 1550 nm.

3. Results

The structural properties of the as prepared glasses have been characterized by Raman spectroscopy using a very low energy (1mW) for the laser excitation at 752 nm to avoid any photoinduced structural changes during these measurements.

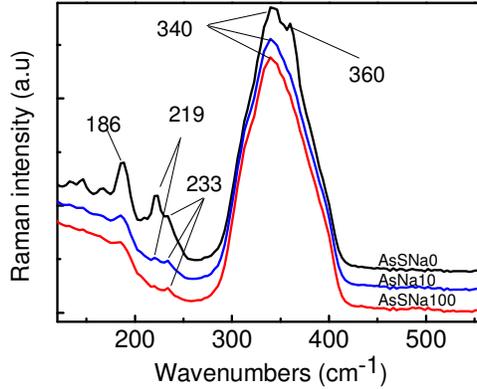


Fig. 1. Raman spectra of the arsenic sulfide initial glasses prepared without NaCl doping (AsNa0), with 10ppm (AsNa10) and with 100ppm (AsNa100) of NaCl doping.

All the Raman spectra exhibit a broad band centered at 340 cm^{-1} attributed to As-S vibrations in $\text{As-S}_{3/2}$ pyramidal sites. When the doping concentration in NaCl decreases, an additional shoulder at 360 cm^{-1} and vibrational modes at 233 , 219 and 186 cm^{-1} can be observed, as shown in Fig. 1. These three additional modes are typical of As-rich compositions and were attributed to As-As homopolar bonds [23–26]. These first data demonstrate that the initial arsenic sulfide glasses under study differ mainly from their stoichiometry in sulfur.

Actually, based on our previous results [22], for AsNa0 samples, due to peculiarity of the distillation procedure, losses of sulfur is around 1-3 atomic% from the stoichiometric one. It results an arsenic rich glass for AsNa0 samples as confirmed by the above Raman spectra. According to SIMS analysis, there is almost no Na^+ ion in AsNa0 samples, and the concentration of Na^+ ions were increased obviously from AsSNa10 to AsSNa100 samples.

The SHG response of the poled samples was tested directly after the poling treatments. Using the first poling configuration, i.e. when the arsenic sulfide glass was in between two n-doped silicon electrodes, we have recorded no SHG signal for all the glass compositions studied. However, for the second kind of poling process (soda lime glass slides ($100\mu\text{m}$ thick) introduced between the n-doped silicon electrodes and the arsenic sulfide glass slide), SHG signals were observed.

The Maker fringes patterns (θ scans) measured for the poled arsenic sulfide glasses are depicted in Fig. 2. One should first notice that the signal recorded for the AsSNa0 sample is (i) not a symmetric function of θ and (ii) is not reproducible as two scans measured successively at the same point give two distinct patterns. For the poled sample AsSNa100, the fringe patterns are symmetric in function of θ and do not vary significantly between two sets of measurements obtained using the shutter mode on (for details see experimental details).

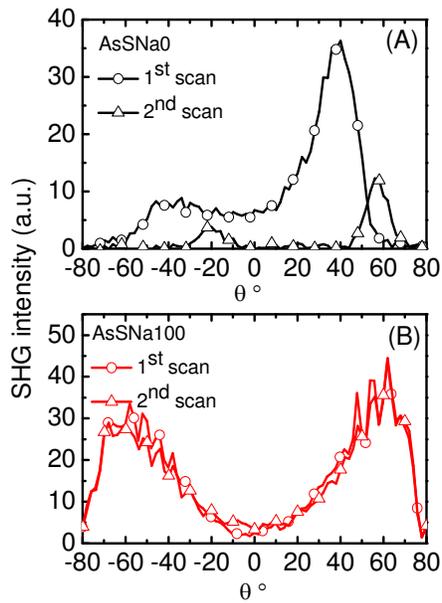


Fig. 2. θ scans measured on samples AsSNa0 (A) and AsSNa100 (B).

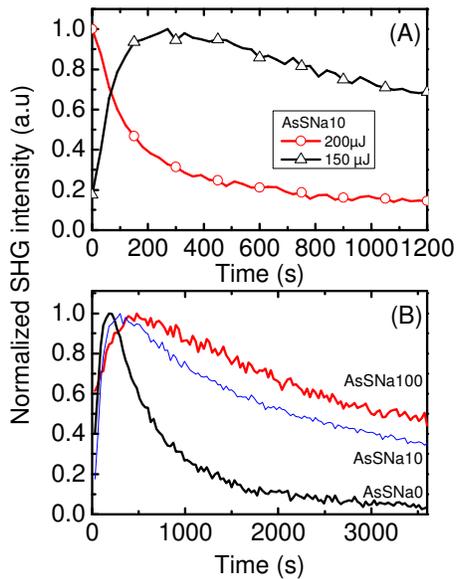


Fig. 3. SHG kinetic measurements for the AsSNa10 poled sample under irradiations @ 1550 nm with 200 μJ and 150 μJ (A) and for poled samples AsSNa0, AsSNa10 and AsSNa100 under irradiations @ 1550 nm with 150 μJ (B).

The stability of the SHG response has been tested by SHG kinetic measurements with a sustained laser irradiation at 1550nm (same laser used to probe the SHG intensity). In Fig. 3, we have summarized the results obtained for one given composition in function of the laser

energy and for all compositions with the same irradiation conditions. The first set of data clearly demonstrates that the SHG response for the poled AsSNa10 is not stable in time under irradiation at 1550 nm with energy of 200 μJ and 150 μJ . For the lower irradiation energy, we first notice a large increase of the signal during the first three minutes of the experiments followed by a slower decrease. At higher energy, we were not able to follow the initial SHG increase but only a quasi-exponential decrease. Comparing the behavior of the different compositions under the same irradiation conditions we observe for all an initial increase followed by a decrease of the SHG response. After 2000 seconds of irradiation, the AsNa0 sample has lost 90% of its SHG signal as compared to drops of 50% and 33% for the AsNa10 and AsNa100 samples respectively.

The photoinduced structural changes of the arsenic sulfide glasses have been characterized by Raman spectroscopy before and after poling. We have used a similar approach as reported by Efimov et al. [9]. We used a continuous 10 mW laser line @752 nm to irradiate the surface of an arsenic sulfide sample and using this laser excitation we have recorded the Raman spectra in real time during the exposure.

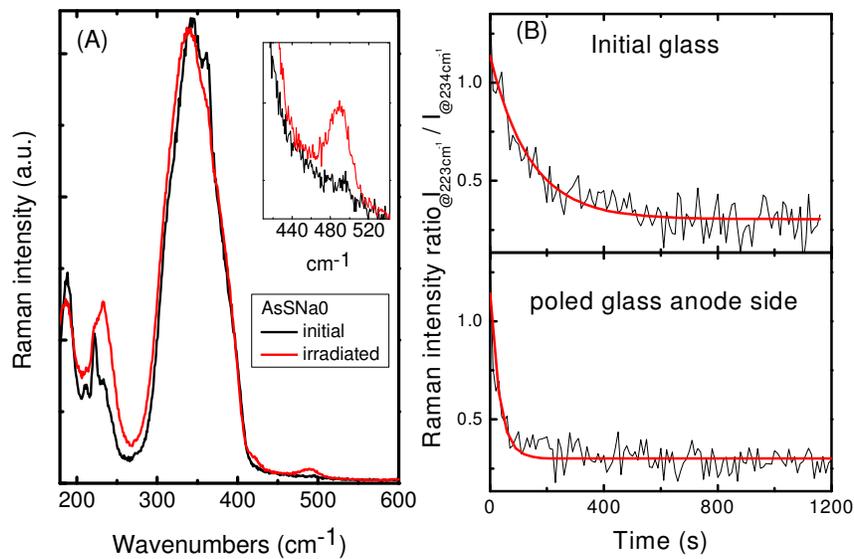


Fig. 4. (A) Raman spectra of an AsSNa0 sample before and after an irradiation of 30 min @ 752 nm with 10mW. (B) Raman intensity ratio ($I_{@223\text{cm}^{-1}}/I_{@234\text{cm}^{-1}}$) measured during the irradiation process for an initial AsSNa0 sample (up) and a poled AsSNa0 sample.

As shown in Fig. 4(A), the irradiation procedure has induced several spectral variations: (i) a shift to lower frequency of the main band at 340 cm^{-1} and an intensity decrease of the shoulders at 360 cm^{-1} (ii) the appearance of two small bands at 415 and 490 cm^{-1} (iii) the relative intensity of the Raman bands at 220 and 230 cm^{-1} is inverted with an intensity increase of the band at 230 cm^{-1} . The same behavior was observed for both initial and poled arsenic sulfide samples. A comparison of the photoinduced structural rearrangements kinetics are shown in Fig. 4(B) by plotting the Raman intensity ratio $I_{@223\text{cm}^{-1}}/I_{@234\text{cm}^{-1}}$ in function of the irradiation time. Under our experimental conditions, the equilibrium of the photochemical process is reached after 800 seconds for the initial glass and for less than 200 s for the poled sample.

4. Discussion

Photoinduced structural rearrangements

Several different models have been developed in the literature to describe photoinduced modifications in optical and structural properties of arsenic sulfide glasses. The existing models can be classified in the following major categories (i) twisting of chalcogen atom bonding [11,12] (ii) bond breaking and structural rearrangements [18,19] (iii) macroscopic electronic charging and formation of charged defects [13,14].

The spectral variations observed in this work clearly state that structural rearrangements are one of the predominant aspects of the photoinduced mechanisms. In the model developed by Shimakawa et al. structural rearrangements are initiated by the formation of photo-excited electrons and holes charged centers which are non-stable (called “intimate pairs” [13,14]). The bonds dissociation occurs in a second step and permits to separate the charged centers and forms a metastable state after the irradiation process.

Spectral variations reported in our study are of particular interest for the cases of arsenic-rich sulfide glasses. The initial glass network can be sketched as a majority of $\text{AsS}_{3/2}$ pyramids arrangements with a significant number of homopolar As-As bonds. These homopolar bonds, which are at the origin of the Raman modes at 190, 220 and 360 cm^{-1} , could be observed either in isolated/molecular As_4S_4 units or in $\text{As}_2\text{S}_{4/2}$ arrangements in which the homopolar bond is connected to the rest of the glass network through sulfur atoms.

In the literature, previous Raman and X-ray studies have described the induced structural rearrangements as a local dissociation of As-S bonds and the formation of homopolar bonding:



After the irradiation process, we can observe an intensity increase of the band linked to S-S bonding at 490 cm^{-1} which is in agreement with the global model described above. This should necessary induce an increase of the number of As-As homopolar bonds in the glass network. Nevertheless, we do not observe a simple intensity increase of the modes linked to structural units with homopolar As-As bonding originally present in the glass. We can particularly notice a new mode at 230 cm^{-1} indicating that the arsenic rich structural units induced by the irradiation process differ from the ones of the initial glass. It is well known by the mineralogist community that visible light exposure can induce a phase change from the realgar to the pararealgar crystalline phase (Fig. 5) [26–28].

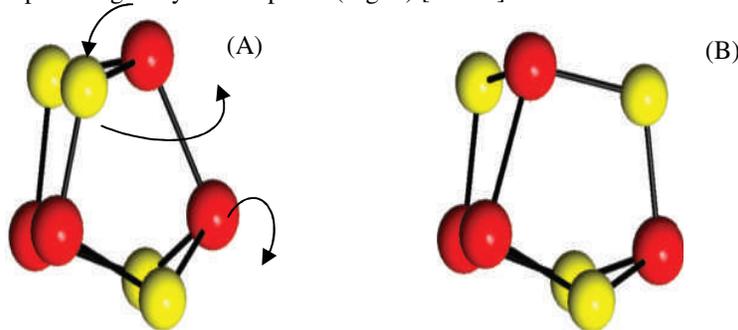


Fig. 5. As_4S_4 molecule transition from realgar-type (A) to pararealgar-type (B) (fig. from [27]).

An accurate Raman investigation of the phase change from the realgar to the pararealgar form has been done by Muniz-Miranda et al. [26] in which the spectral variations observed are similar to the one observed in our work, i.e. a decrease of the modes at 360, 219 and 186 cm^{-1} attributed to realgar-like structural units and an increase at 230 cm^{-1} which is typical of pararealgar-like arrangements. Nevertheless, as realgar and pararealgar molecular entities are

As₄S₄ polymorph, it is important to point out that a simple change of As₄S₄ polymorph molecular units cannot explain how S-S bonds are formed after irradiation. One possibility is that the homopolar As-As bonds are not present in the glass as isolated As₄S₄ units but as As₂S_{4/2} arrangements linked to the rest of the network. Then the irradiation should form As-As-As linkage similar to the one present in the pararealgar structure (Fig. 5). Finally, a molecular description of the photoinduced structural rearrangements could be pictured as shown in Fig. 6.

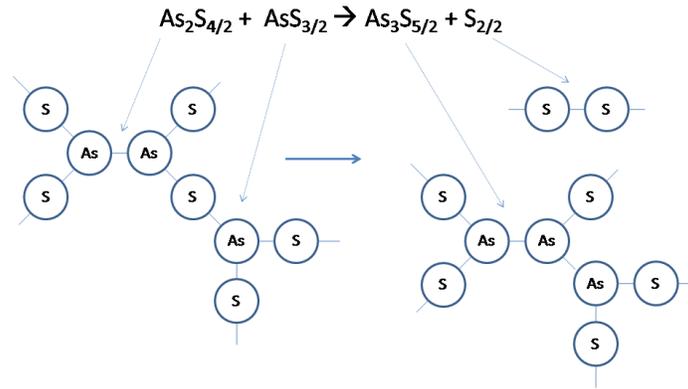


Fig. 6. Tentative of molecular model for the photoinduced structural changes in Arsenic rich sulfide glasses.

This tentative model could describe the spectral variations observed as it predicts (i) a decrease of the As-As initial homopolar bonds (i.e. As₂S_{4/2} units and Raman bands at 190, 220 and 360 cm⁻¹) (ii) the formation of pararealgar like structural arrangements (i.e. As₃S_{5/2} units and Raman bands at 230 cm⁻¹) and (iii) the formation of S-S bonding (i.e. S_{2/2} units and Raman bands at 490 cm⁻¹). Some theoretical calculations are in progress to confirm our assumptions. Nevertheless, one first conclusion of our study is that in arsenic-rich sulfide glasses, structural motifs close to a realgar unit assist the proliferation of the photoinduced changes. These photoinduced structural changes appear to be similar to what has been observed and well described in mineralogy with the study of As₄S₄ polymorphs. In addition, such hypothesis of mid-range glass structure modification have been mentioned by different authors, Pfeiffer et al. has in 1991 claim that the presence of As-As cannot be alone responsible for the photodarkening and that mid-range structure modification should be involved [29].

Poling mechanisms and photoinduced processes

Concerning correlations between poling and irradiation processes in arsenic sulfide compositions, our study have shown that (i) a poling treatment has a strong influence on the kinetic of photoinduced structural rearrangements and (ii) the second harmonic generation signal temporal evolution is highly dependent on both the arsenic content in the glass and the light intensity used during the measurement.

To describe the poling mechanisms, one should remind that no SHG signal was observed under blocking anode conditions (i.e. Silicon wafer at the anode side of the poled glass; in this condition we neglect charge injection at the anode interface). A SHG signal was observed if we used soda lime glasses at the anode and cathode sides. Under this poling configuration, the anode interface of the arsenic sulfide sample should be considered as an open electrode and the mobile species from the soda lime glass slide, such as sodium ions, are expected to be injected from the soda lime glass slide within the arsenic sulfide network. In such a configuration, the origin of the space charge implemented during the poling process should originate from a field-assisted ions diffusion process. In the classical model developed for

oxide ionic glasses, the electric field implemented is due to a large difference of electrical resistivity between the bulk and the ions exchange layer [30]. In our case, arsenic sulfide glass samples are either free of mobile ions or doped at a very low content (100 ppm or less). Thus, one cannot consider the sodium ions injection in such glass compositions as a classical ions exchange. To compensate positive charge injections, it is necessary to consider the formation of negative charges which could originate from electron/holes charge defects creation within the arsenic sulfide network.

In addition, SHG responses observed have shown that two contributions should be considered: (i) the classical EFISH process linked to the electric field implementation during the poling treatment which can be attributed to the clear interference patterns measured for the sample AsNa100 (Fig. 2(B)) [31] and (ii) possible photoinduced effects at the origin of the evolution of the SHG intensity i.e. a fast increase of SHG signal followed by a gradual intensity decrease occurring under the irradiation at 1550 nm used for SHG measurements. It has to be noted that the signal occur in the transparent region of the glass, thus we assume that at this wavelength the changes in linear optical properties induced by photodarkening effects could not explain the large variations observed on the SHG response (80% of SHG signal increase for the AsNa0 and AsNa10 samples in Fig. 3). In the case of photoinduced SHG, the excitation wavelength at 1550 nm is far from the absorption band gap of the studied materials. Moreover, under our experimental conditions (100-200 μJ @ 1550 nm nanosecond pulses), photo induced SHG has been observed only within the polarized area. One would remind that in this class of glasses the optical illumination is expected to induce first charge defects (self-trapped excitons) followed by bond switching reactions leading to structural rearrangements. Thus, it could be considered that the photoinduced SHG response measured in arsenic sulfide polarized glasses as a multi-photon process assisted by the charge defects created during the poling treatment. This conclusion should be related to the results obtained by Raman spectroscopy (Fig. 4) showing the faster kinetic of the structural rearrangements induced by irradiation in the polarized glass as compared to the initial glass. In addition, it could also be correlated to the data reported by Shimakawa and al. on the acceleration of photodarkening and photoinduced fluidity under dc electric field [32,33].

Finally, one should discuss the origin of the photoinduced nonlinear optical response and its stability. Photoinduced anisotropic structure has been reported which could be at the origin of a SHG signal [16]. However, in such a case one may expect this anisotropic structure to be stable under irradiation. As we have always observed a gradual decrease of the SHG signal under illumination, we may explain the photoinduced SHG activity by the formation of local dipoles linked to charge defects formation and/or displacement. As expected the charge defects should be then compensated by structural rearrangements. This could explain first the increase of the SHG response by an increase of the number of charge defects inducing important local dipoles and then the decrease of the SHG signal induced by a gradual compensation of these dipoles by bond switching and the formation of new neutral structural entities. This charge compensation process permits also to explain the low stability of the SHG response induced by thermal poling. In the present case, the different glasses exhibit prior poling and irradiation different amount of homopolar bonds. As previously mentioned, these homopolar bonds could be considered as initiator of the photoinduced processes. Thus, the large differences observed in the SHG kinetic should be also explained by differences in sulfur stoichiometry which directly influence the effectiveness of charge defects formation and structural rearrangements induced by illumination.

5. Conclusion

We have observed photoinduced SHG in thermally poled arsenic sulfide glasses. Thermal poling permits to assist this photoinduced nonlinear optical response by the formation of charge defects in the glass network. A mechanism for observed photoinduced structural rearrangements is proposed, consistent with the Raman analysis of samples. This mechanism involved the formation of pararealgar like units and S-S bonding formation.

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