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Second harmonic generation in poled tungsten tellurite glasses

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Second harmonic signals have been successfully generated in thermally poled 85%TeO₂–15%WO₃ glasses. Thermal poling of these glasses was undertaken at various temperatures and heating times using a voltage of 4.5 kV. The sample thickness was 500 μm. Second harmonic generation (SHG) in the poled glasses was analysed using the Maker fringes technique. After optimisation of the poling conditions (T=280°C, t=1 h), high χ⁽²⁾ values (about 1.6 pm/V) were obtained. It was demonstrated that this thermal poling treatment has generated optically nonlinear zones on the anodic surface. The thickness of the surface layer given a SHG was thin (5.22 μm), as classically observed with tellurite glasses. The possible reorientation, under electric field, of the glass structural entities could be the origin of such second order nonlinear properties.

Increasing interest in materials with nonlinear optical properties has been induced by the important industrial request for optical and electro-optical devices. Glasses are very good potential candidates for such applications because of their formability and their chemical stability. More particularly, tellurium dioxide based glasses are of special interest as their compositions can be readily adjusted due to their large glassy domains; they have low melting temperatures, good visible and infrared light transmittance, weak absorption coefficients and especially high linear (n_0) and nonlinear (n_2 , χ^3) indices.⁽¹⁾ The stereochemical activity of Te(IV) atoms is certainly at the origin of such properties. It is very often reinforced when either a second lone pair holder (Tl⁺, Bi³⁺ ...) or a d⁰ cation (Nb⁵⁺, W⁶⁺ ...) is associated with the Te(IV) atoms.^(1–3)

Nonlinear optics involves the study of phenomena induced by a modification of optical properties of a dielectric material under an intense beam. Basically, the nonlinear optical properties of transparent materials result from the generation of a polarisation P when an intense electromagnetic wave enters into these materials under an electric field E . This polarisation P can be expressed as a power series in the electric field E

$$P = P_0 + \chi^{(1)}E + \chi^{(2)}EE + \chi^{(3)}EEE + \dots$$

where P_0 is the permanent polarisation, $\chi^{(1)}$ is the linear susceptibility which accounts for the linear optical index. $\chi^{(2)}$ and $\chi^{(3)}$ correspond, respectively, to the second and third order nonlinear susceptibilities. For a high intensity oscillating field E with frequency ω , the second term is responsible for the generation of a double frequency 2ω oscillating field, called second harmonic generation (SHG). This can appear only in non-centrosymmetric materials in which the second order nonlinear susceptibility $\chi^{(2)}$ is different to zero. Amorphous materials, such as glass, with an inversion symmetry at the macroscopic scale do not in principle generate second order optical nonlinearities. Nevertheless, it is now well recognised that is possible to break the inversion symmetry at a microscopic scale through a technique such as thermal poling and thus to induce second order nonlinearity. Thermal poling consists in applying a dc electric field at an elevated temperature (below the transition glass temperature T_g) and cooling the glass before removing the voltage.⁽⁴⁾ The mechanism underlying the formation of the nonlinearity in bulk glass is not yet completely understood. According to Myers *et al*, two different mechanisms can account for the induced second order nonlinear susceptibility: charge migration or dipole reorientation.

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The model based on these two mechanisms can be expressed as^(4,5)

$$\chi^{(2)} \propto \chi^{(3)} E_{dc} + (Np\beta^*/5kT) E_{loc}$$

The first term is related to the interaction between the residual electric field E_{dc} inside the material after removing the applied dc field and the third order nonlinearity. The second term is the resulting macroscopic second order nonlinearity induced by reorientation of polar bonds during poling treatment, each of them with a permanent dipole moment p (N is the number of permanent dipoles) and an hyperpolarisability β^* , subject to a local field E_{loc} .

Over the last ten years, it has been demonstrated that poling can induce second order nonlinearity in various tellurite glasses such as $\text{TeO}_2\text{-ZnO}$,⁽⁶⁻⁸⁾ $\text{TeO}_2\text{-WO}_3$,^(6,9) $\text{TeO}_2\text{-B}_2\text{O}_3$,⁽¹⁰⁾ $\text{TeO}_2\text{-Nb}_2\text{O}_5$,^(11,12) $\text{TeO}_2\text{-Nb}_2\text{O}_5\text{-Li}_2\text{O}$,⁽¹³⁾ $\text{TeO}_2\text{-Na}_2\text{O-Li}_2\text{O}$,⁽¹⁴⁾ $\text{TeO}_2\text{-ZnO-MgO}$,^(10,15) $\text{TeO}_2\text{-ZnO-Na}_2\text{O}$ ⁽¹⁶⁾ and $\text{TeO}_2\text{-Pb(PO}_3)_2\text{-Sb}_2\text{O}_3$.⁽¹⁷⁾ The second order nonlinear susceptibilities, $\chi^{(2)}$, measured were generally in the range 0.1 pm/V ($\text{TeO}_2\text{-ZnO-MgO}$ glasses)⁽¹⁰⁾ – 0.9 pm/V ($\text{TeO}_2\text{-ZnO}$ glasses),⁽⁸⁾ except for 80 $\text{TeO}_2\text{-20WO}_3$ (mol%) glass for which a very high $\chi^{(2)}$ of 2.1 pm/V was obtained.⁽⁹⁾

Up to now, the most reliable models to explain the origin of SHG in tellurite glasses are based on either the migration of charged impurities,^(8,11,12,18) e.g. Na^+ , towards the cathode side glass of the poled material or the possible reorientation,^(6,7,10,15,16) under the electric field, of the asymmetrical (TeO_n) structural units (where n varies from $n=3$ or 4 depending on the composition of glasses) in glassy samples with electric dipoles. This article aims to report SHG investigations, using thermal poling, on a 85 $\text{TeO}_2\text{-15WO}_3$ (mol%) compositional glass. The choice of this composition takes the following points into account: it has a good thermal stability, a high mechanical strength⁽¹⁹⁾ and an expectedly high third order nonlinear susceptibility $\chi^{(3)}$. Moreover, this composition can be crystallised on heating to give the non-centrosymmetric metastable $\gamma\text{-TeO}_2$ phase which exhibits SHG.^(20,21) Studies are now in progress to control the crystallisation of $\gamma\text{-TeO}_2$ phase nanoparticles in the bulk 85 $\text{TeO}_2\text{-15WO}_3$ (mol%) glass to promote SHG. These results on glass ceramics will be reported in a future paper. The present study details an investigation into SHG in 85 $\text{TeO}_2\text{-15WO}_3$ (mol%) glass, via an optimisation of the thermal poling conditions. The structural properties of the poled and unpoled glasses were studied using Raman spectroscopy. X-ray microprobe analyses were performed on both surfaces of the poled glasses.

Experimental

Glass preparation

85 $\text{TeO}_2\text{-15WO}_3$ (mol%) glasses were obtained using appropriate quantities of reagent grade TeO_2 and WO_3 (commercial product Interchim, +99%) as starting materials. TeO_2 was prepared by the decomposition at 550°C of commercial H_6TeO_6 (Aldrich 99.9%). A small amount of Sb_2O_3 (2 mol%) was added in order to lighten the glasses. Glassy pellets were prepared by melting the powder mixtures in platinum crucibles, at 800°C for 30

min. The melts were then rapidly quenched by flattening between two preheated brass blocks separated by a brass ring. This produced cylindrical samples 10 mm in diameter and 1.5 mm thick. The glasses were annealed at 300°C for 10 h (about 40°C below their glass transition temperature of 344°C) to remove the thermal stresses induced in the as quenched glasses. The samples were then mechanically polished to give 500 μm thick planar disks with parallel faces suitable for optical measurements. The resultant glasses were pale yellow and transparent as expected. Their homogeneity was checked using optical microscopy.

Thermal poling

The glass disks were thermally poled by using a home made apparatus. The 500 μm thick glass was sandwiched between two thin commercial borosilicate plates and kept in contact with stainless steel electrodes equipped with a heating stage. This equipment was placed inside a vacuum chamber. Different poling conditions were investigated. The glassy samples were heated up to temperatures ranging from 250°C to 310°C under a vacuum of about 10^{-5} torr. After stabilisation of the temperature, a dc poling voltage was applied under different conditions (voltage from 3–4.5 kV, poling time from 20 min to 8 h). Then the glasses were cooled slowly to room temperature whilst maintaining the voltage and the vacuum. The voltage was switched off once the samples reached the room temperature.

Optical measurements

The optical transmission spectra of the unpoled and poled glasses were recorded at room temperature using a double beam spectrophotometer (AFAS-Monaco) in the wavelength range 400–1000 nm.

The second harmonic generation intensity of the thermally poled glasses was measured using the Maker fringes method. This method consists of varying the angle between the incident laser beam, with frequency ω , and the glass sample containing at least one nonlinear optical planar layer. The intensity of the transmitted and generated 2ω optical signal was then recorded by changing the angle in a periodic fashion. Simulations of the Maker fringes spectrum enables estimation of the second order nonlinear coefficient d_{33} and the thickness of the nonlinear zone. It is worth noting that the nonlinear coefficient d_{33} is directly linked to the second order susceptibility $\chi^{(2)}$ by $d_{33} = \frac{1}{2}\chi^{(2)}$.⁽²²⁾

The SHG Maker fringes were analysed using a new general ellipsometrical analysis for planar multilayered systems.⁽²³⁾ The whole Maker fringe signal is recorded for two polarisation configurations: pp and sp polarisation, where pp and sp refer to the linearly polarised incident beam with a polarisation parallel to the plane of incidence (pp) or with a polarisation perpendicular to the plane of incidence (sp).

The set up for SHG measurements is shown in Figure 1. It was composed of a Q-switched Nd/YAG laser operating at a wavelength of 1064 nm with a 30 Hz repetition rate and a 10 ns pulse width. A beam attenuator placed just after the laser source enabled adjustment of the pulse energy at the sample. The po-

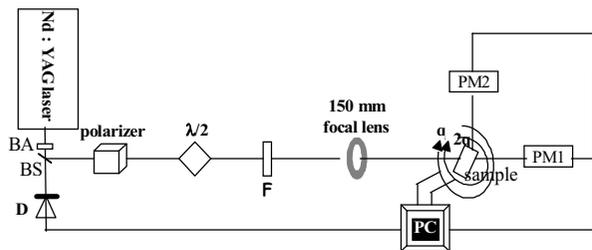


Figure 1. Schematic diagram of the experimental setup for SHG acquisitions: BA: beam attenuator; BS: beam splitter; D: near infrared diode; F: 1064 nm filter or LiNbO₃ crystal and 532 nm filter; PM1: 532 nm filter, analyser and photomultiplier tube; PM2: 532 nm or 1064 nm filter, analyser and photomultiplier tube. The first detection unit PM1 enables the transmitted SHG signal to be detected, and a coupled rotation (2θ) of the second detection unit PM2, with respect to the sample angle (θ), enables reflection measurements to be undertaken

larised source beam was split into two rays by a beam splitter: one ray was used to record the fundamental (ω) intensity using a near infrared diode detector; the other, which was firstly polarised by a glan polariser, passed through a half wave (1064 nm) rotation plate and a set of appropriate filters and then was focused on the sample with a spot of 10 μm diameter. The harmonic (2ω) transmitted signal was collected by a detection unit consisting of a 1064 nm selective reflector, a bandpass filter (532 nm), a rotation analyser and finally a photomultiplier tube. The reflected fundamental or harmonic wave was simultaneously collected by a second detection unit with a double goniometer θ - 2θ coupling. Because data may contain errors due to fluctuations between laser pulses, the collected intensities were averaged over 100 pulses. Absolute calibration of the SHG intensities was obtained using z-cut quartz and taking $\chi_{11}=0.6$ pm/V as a reference.⁽²⁴⁾

This setup also has enabled estimation of the linear refractive index at ω and 2ω by collecting the 2θ reflected wave around the Brewster angle over the [15–80°] θ range. A LiNbO₃ crystal in phase matching condition was used as a 532 nm source to record the reflected signal. It is very important to determine two linear refractive indices at 1064 and 532 nm because these values indicate the dispersion in the indices and provide a very good indication of the coherence length of the material.

Surface characterisation

Structural studies of the poled glasses were undertaken using Raman scattering. The Raman spectra were recorded in the 100–1200 cm^{-1} range using a Dilor spectrometer (XY model), equipped with a CDD detector and an Ar⁺ laser (514.5 nm excitation line) in a back-scattered geometry. The diameter of the laser spot focused on the sample was about 1 μm . Measurements were made at low power (<100 mW) of the excitation line, in order to avoid any damage to the samples. The spectral resolution was about 4.5 cm^{-1} at the excitation line.

Quantitative compositional analysis was undertaken using an X-microprobe in EDS (energy dispersion spectroscopy) mode on both surfaces of the poled glass. Measurements were made with a 40 nA electron beam

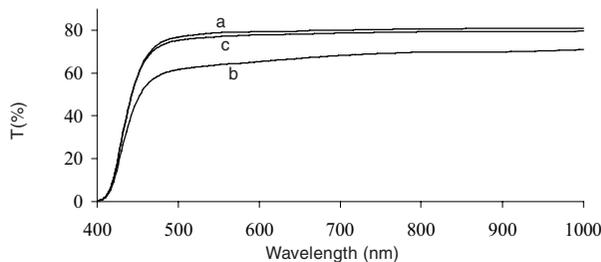


Figure 2. Optical transmission spectra of the 85TeO₂-15WO₃ (mol%) glass: (a) unpoled glass; (b) poled glass; (c) poled glass polished on cathode side

and an accelerating voltage of 20 kV, corresponding to a sodium detection limit of 340 ppm (0.0340 wt% or 0.085 at%). The diameter of the electron beam was 10 μm .

Results and discussion

Ultraviolet-visible absorption and linear refraction indices

The optical transmittance of the glass is an important parameter to determine before beginning simulation of the measured second harmonic signal because it gives information about the dispersion inherent in the material. The 85TeO₂-15WO₃ (mol%) glass has a large domain of transparency which varies from 500–1000 nm (Figure 2(a)). Nevertheless, thermal poling blackens the surface on contact with the cathode which increases the ultraviolet-visible absorption of the glass due to reflection losses or 'lost' diffusion (Figure 2(b)). After a slight polishing of this face, the glass recovers its properties (Figure 2(c)) and the second order non-linearity is conserved. Moreover, the maximum of transmission stabilised at 80%, is due to many reflections at the glass faces. This transmission maximum indicates that this glass should possess high linear refractive indices ($n_0 > 2$) as classically observed with tellurite glasses. This is confirmed by measurement of these indices using the Brewster angle reflection method: $n_0=2.193(\pm 0.001)$ for the wavelength 532 nm and $n_0=2.087(\pm 0.001)$ for the wavelength 1064 nm.

Second harmonic generation

As SHG in 85%TeO₂-15%WO₃ glasses has never been studied, different thermal poling conditions (temperature and time) have been investigated to optimise the second harmonic signal. Second order nonlinear coefficients d_{33} deduced from Maker fringe simulations and the nonlinear zone depths are reported in Table 1 for different poling conditions. Significant second harmonic signals were observed for all poling conditions. The surface SH active layer (3–17 μm) was obtained at the anode side.

No coherence is observed between the different values of the d_{33} coefficient and the depths of the nonlinear zone. These results are not evidence of real evolution with respect to the poling temperature or the poling time. Nevertheless, some main features can be underlined. The values of the d_{33} coefficients are about 0.3–0.4 pm/V, which are high values compared to those of other tellurite glasses or oxide glasses. The best compromises lie in a poling temperature about 50°C lower

Table 1. Second order nonlinear coefficient (d_{33} : $d_{33}=\frac{1}{2}\chi^{(2)}$) and SH layer thickness (L), for different thermal poling conditions, of glasses with 85TeO₂-15WO₃ (mol%) composition (voltage: 4.5 kV and thickness of samples: 500 μm)

Poling condition		d_{33} (pm/V) (±0.01)	L (μm) (±0.01)
Temperature	Time		
250°C	4 h	0.34	17.07
	8 h	0.27	16.68
	2 h	0.35	3.50
265°C	4 h	0.30	3.24
	8 h	0.33	1.50
	20 min	0.43	3.80
280°C	1 h	0.79	5.22
	2 h	0.40	12.00
	30 min	0.41	3.42
295°C	1 h	0.42	3.20
	2 h	0.31	3.19
	1 h	0.42	16.73

than the glass transition temperature T_g (344°C) and a poling time that is not too long, but is long enough to obtain an electric equilibrium under the electric field (1 or 2 h). For too high poling temperatures (>300°C) or too long poling times (>2 or 4 h with respect to the heating temperature), glasses are damaged by fracture and/or blackening. The highest value of the d_{33} coefficient was obtained under the following optimised conditions of poling: 280°C for 1 h under a dc voltage of 4.5 kV. Figure 3 shows experimental and simulated Maker fringes for these poling conditions. The corresponding second order nonlinear susceptibility χ^2 is 1.6 pm/V, one of the highest values ever observed in tellurite glasses. This value can be linked to the third order nonlinear susceptibility χ^3 which is very high for this glass ($\chi^3 \approx 300 \times 10^{-23}$ m²/V², measured at $\lambda = 0.8$ μm). The SH active layer is very thin ($L = 5.22$ μm).

The chemical compositions of an unpoled glass and of two glasses poled under extreme conditions (heating at 250°C for 8 h and heating at 295°C for 30 min), have been checked using an x-ray microprobe. Both surfaces of the poled glasses, that are in contact with electrodes during the poling process, have been analysed. The values reported in Table 2 are average ones and it is important to underline that the percentage of each element present has shown no variation along the anode or the cathode surfaces. These analyses clearly show that no noticeable modification of glass compo-

Table 2. Percentages of different atoms constituting the 85TeO₂-15WO₃ poled glass (esd are given in parentheses)

Atom	Before poling	Poling conditions		295°C, 30 min	
		250°C, 8h Anode (at%)	Cathode (at%)	Anode (at%)	Cathode (at%)
Te	27.2	27.0(2)	27.2(2)	27.1(2)	27.3(2)
O	68.2	67.9(6)	68.2(6)	68.0(6)	68.2(6)
W	4.6	4.5(2)	4.6(2)	4.5(2)	4.5(2)
Na	0	0.52(5)	0.01(5)	0.44(5)	0.02(5)

sition occurs after poling. In the two poled samples, the appearance of a significant amount of sodium at the anode side can be observed. Sodium was only observed on the anode side (atomic percentage > detection limit of sodium) and not on the cathode side (the atomic percentage of Na could not be extracted from the measurement noise). Moreover a cross sectional analysis of these samples has not shown any Na⁺ composition gradient from the anode side towards the cathode side. The sodium at the anode side, which is relatively low, is certainly due to diffusion from the borosilicate plate through the face in contact with the anode during the poling treatment. These results indicate that, no Na⁺ cations migrate from the anodic side towards the cathodic side, contrary to what has been previously observed in other tellurite systems^(8,11,12,18) and under different poling conditions.

The Raman spectrum of the 85TeO₂-15WO₃ (mol%) glasses is shown in Figure 4. This spectrum is quite similar to the Raman spectrum of pure TeO₂ glass.⁽²⁵⁻²⁷⁾ It has two main bands situated near 450 and 650 cm⁻¹, which correspond respectively to the symmetric vibrations of the Te-O-Te bridges and to the asymmetric vibrations of the Te-O terminal bonds, both co-existing in TeO₂ glass. This indicates that the glassy network is mainly comprised of TeO₄ units. The band located near 930 cm⁻¹ corresponds to W=O stretching vibrations. No significant differences can be observed between the spectrum obtained from an unpoled sample and the spectrum obtained from a poled sample (Figure 4). It is worth noting that the spectra recorded on both faces of the poled glass are identical. The only weak difference between spectra of the unpoled and poled glasses can be seen on the broad

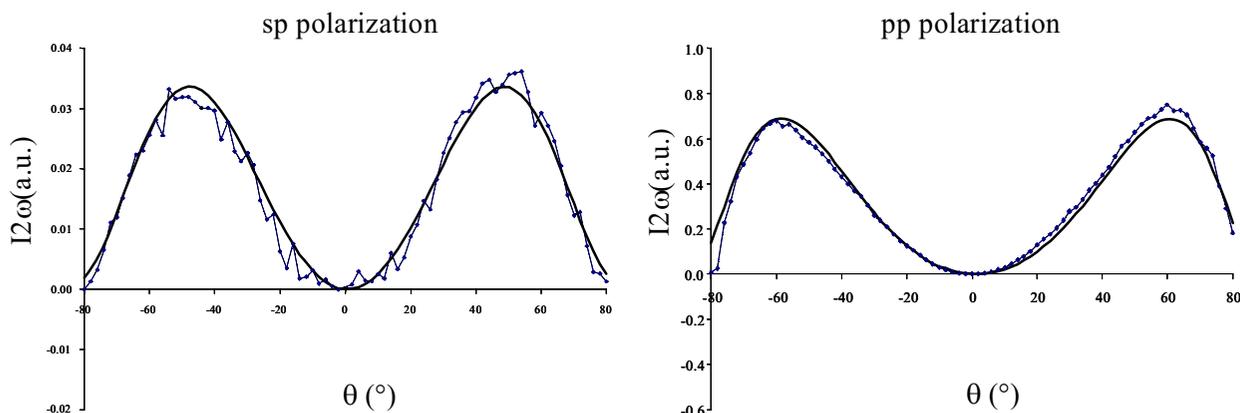


Figure 3. Experimental (lines with circles) and simulated (continuous lines) Maker fringes for the 85TeO₂-15WO₃ (mol%) glass poled at 280°C for 1 h under a voltage of 4.5 kV

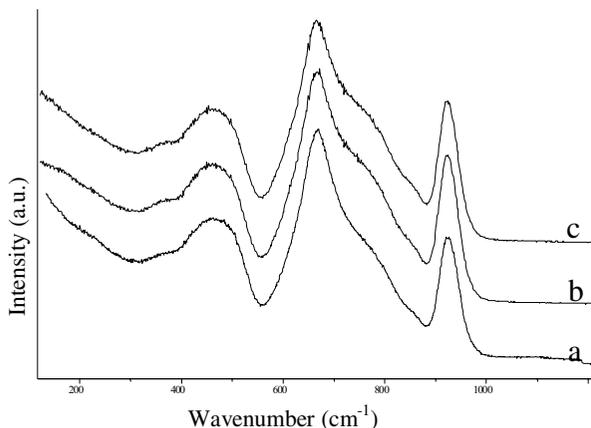


Figure 4. Raman spectra of the 85TeO₂-15WO₃ (mol%) glass: (a) before poling; (b) after poling on anode side; (c) after poling on cathode side

band situated in the range 700–800 cm⁻¹, which is attributed to the asymmetric vibrations of the Te–O terminal bonds. The intensity of this band seems to have slightly increased after poling. This could mean that no significant structural modification is induced by thermal poling (TeO₄ units are conserved, no breaking of the tellurite glass network, only the Te–O terminal bonds are involved) and that only a reorientation of these glass structural TeO₄ entities occurs under electric field. The presence of a 5s² electronic lone pair on Te(IV) atoms certainly enhances this reorientation. This mechanism could be at the origin of the SHG in tungsten tellurite poled glasses.

Conclusion

85TeO₂-15WO₃ (mol%) glasses have been poled and have shown a better SHG performance than silicate glasses (generally <1 pm/V) and most other tellurite glasses. After optimisation of the thermal poling conditions, a high second harmonic signal ($\chi^{(2)}$ =1.6 pm/V) was obtained under the following conditions: $T=280^{\circ}\text{C}$, $t=1$ h, $V=4.5$ kV. The surface SH active layer was thin (5.22 μm) and occurred at the anode side. Both poled surfaces, in contact with electrodes during the poling treatment, were analysed by Raman spectroscopy and x-ray microprobe analysis. No migration of sodium towards the cathodic surface was found. No significant structural modification was observed, and only a reorientation of the TeO₄ glass structural entities can be the origin of SHG in 85TeO₂-15WO₃ (mol%) glasses.

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