



Materials Research Bulletin



journal homepage: www.elsevier.com/locate/matresbu

Second Harmonic Generation induced by optical poling in new TeO_2-Tl_2O-ZnO glasses

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ARTICLE INFO

Article history: Received 12 December 2009

Accepted 29 January 2010 Available online 6 February 2010

Keywords: A. Glasses D. Optical properties

ABSTRACT

New tellurite glasses with a large glass forming domain were elaborated within the TeO₂-Tl₂O-ZnO ternary system. The evolution of the glass transition (T_g) and onset crystallization (T_0) temperatures for such tellurite glasses was studied, in particular, as a function of the Tl₂O addition. A decrease of both T_g and T_0 temperatures was observed; the former being more affected. Structural modifications induced by the addition of the modifiers were studied by Raman spectroscopy. For a fixed ZnO concentration, the increase in the Tl₂O content leads to a destruction of the glass framework, characterized by the transformation of TeO₄ disphenoids into isolated TeO₃²⁻ trigonal pyramid-like ortho-groups. For a fixed Tl₂O concentration, the ZnO addition induces similar effects on the glass structure. The optical transmission of the ((80 - x)TeO₂-xTl₂O-2OZnO) (x = 10, 20 and 30 mol%) glasses was measured in the 300-2000 nm range. Their good transparency was evidenced and a clear reduction of the optical bandgrap was noticed with the increase in the Tl₂O concentration. The second order non-linearity amplitude is found to be increasing as a function of the Tl₂O concentration, in the tested range.

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1. Introduction

TeO₂-based glasses are among the most promising candidates for integration in non-linear optical devices, such as up-conversion frequency systems, high speed optical-switches, since they exhibit high linear and non-linear refractive indices, good visible and infrared transmittance, high Raman gain performances, and since their third-order non-linear optical susceptibility ($\chi^{(3)}$) is among the highest for oxide glasses [1–8].

Second Harmonic Generation (SHG) should be forbidden in glass due to its isotropy. However, second order non-linearity can be induced in glasses exposed to intense laser light (optical poling) [9,10], or thermally treated under the application of an electric field (thermal poling) [11]. Since then, both photo- and thermoelectrically induced SHG have been reported several times in various glass systems [12–23]. Among that list, some of the articles are of particular interest for us, as their authors focus on thermal and/or optical poling of TeO₂-based glasses containing either Tl₂O or ZnO modifiers: namely TeO₂–ZnO and TeO₂–Tl₂O glasses [14,19,20], or TeO_2 -ZnO-Na₂O, TeO_2 -BaO-ZnO, TeO_2 -ZnO-Li₂O and TeO_2 -ZnO-MgO glasses [19-23].

We start by reviewing the relevant papers where the glass forming domain in TeO_2 –ZnO and TeO_2 – Tl_2O binary systems is studied. Imaoka and Yamazaki, Wogel et al., Kozhukharov et al., as well as Yakhkind reported on the glass forming domain in TeO_2 – ZnO and TeO_2 – Tl_2O systems [24–27]. In addition, in [28], Jeansannetas et al. reinvestigated the TeO_2 -rich part of TeO_2 – Tl_2O system in order to properly establish the glass forming domain, as a large dispersion of glass domain limits was found in the above cited works (see Refs. [25,27]).

As we are extremely interested in the structural characteristics of tellurite glasses, we review now the papers related to the structure of such glasses and to its evolution as a function of the concentration of Tl or Zn oxide modifiers. Mochida et al. showed that the primary structural fragment of tellurite glasses containing high TeO₂ content is a distorted TeO₄ bipyramid, and that the fraction of TeO₃ trigonal pyramids increases with an increase in the mono- or di-valent cations [29]. The structure of MO–TeO₂ glasses (with M being a divalent cation: Mg, Sr, Ba or Zn) [30], as well as the structure of $MO_{1/2}$ –TeO₂ glasses (with M being a monovalent cation: Li, Na, K, Rb, Cs and Tl) [31], was studied by Sekiya et al., using Raman spectroscopy. In [30], they indicated that the

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^{0025-5408/\$ –} see front matter $\ensuremath{\textcircled{o}}$ 2010 Elsevier Ltd. All rights reserved. doi:10.1016/j.materresbull.2010.01.024

structure of MgO-TeO₂ glasses, with low MgO content, is a continuous network composed mainly of TeO₄ trigonal bipyramids (or TeO₄ disphenoids) and TeO₃₊₁ polyhedra. Then, with the addition of MgO, the fraction of tellurium atoms forming TeO₃ trigonal pyramids increases. When the MgO content exceeds 40 mol%, then, isolated structural units, such as TeO_3^{2-} and Te₃O₈⁴⁻ ions, are formed in glasses. Based on the similar shapes of their Raman spectra and a great resemblance of compositional dependences of Raman peak intensities, they assumed that ZnO-TeO₂ glasses have the same structure as those of MgO-TeO₂ glasses. Hence, the structure of ZnO-TeO₂ glasses will be modified in a similar manner with the addition of ZnO. In [31], Sekiya et al. showed that the structure of thallium tellurite glasses with less than 30 mol% TlO_{0.5} is similar to that of alkali tellurite glasses containing equal amounts of $MO_{0.5}$ (with M being Li, Na, K, Rb or Cs). In alkali tellurite glasses, they also observed that the fraction of TeO₄ trigonal bipyramids decreases with increasing alkali content. Thus, the same tendency to break the continuous network constructed by sharing corners of TeO₄ disphenoids is observed with the addition of thallium oxide. Jeansannetas et al. [32], as well as Noguera et al. in [33], also evidenced the progressive transformation of TeO₄ units into island-type TeO₃ ortho-anions with increasing Tl₂O content. They reached then the same conclusions as Sekiya et al. in [31], concerning the depolymerization of thallium tellurite glasses with an increasing Tl₂O content. Jeansannetas et al. reported also on the relationships between the glass structure and the optical non-linearities in TeO₂-Tl₂O glasses. For that particular type of thallium tellurite glasses, they measured one of the highest non-linear refractive index at 1.5 μ m ($n_2 = 9 \times 10^{-19} \text{ m}^2/\text{W}$) [32]. In addition, Soulis et al. detailed the role of the modifier's cation valence on the structural properties of various TeO₂-based glasses, and in particular, for TeO₂-Tl₂O glasses [34]. Like Sekiya et al. [31], they also attributed each Raman band to a specific vibration. We simply mention as well that the structure of TeO₂-ZnO glasses was investigated by Shimizugawa et al., using another technique than Raman spectroscopy: EXAFS [35].

We will list finally, not exhaustively, other studies of interest for us and which are focused on glass forming domain, structural investigations, and linear or non-linear optical properties of glasses elaborated mainly within TeO2-ZnO- and TeO2-Tl2Obased ternary systems. Berthereau et al. published the thermal properties, the densities, as well as the optical properties (linear $(n_0 \text{ and optical transmission})$ and non-linear refractive indices (n_2)) of various TeO₂-based glasses, and in particular, of binary TeO₂-ZnO glasses [36]. Chagraoui et al. have evidenced a small glass forming domain in the ZnO-Bi₂O₃-TeO₂ system [37]. Recently, Udovic et al. published the formation domain, and the thermal and structural characterizations of new glasses within the TeO₂-TiO₂-Tl₂O system [38]. In particular, they studied the role of Tl₂O and TiO₂ modifiers on the glass structure and on the physical properties. It was found that Tl₂O favours the nonlinear optical properties, whereas TiO₂ improves their thermal and mechanical stabilities. Dutreilh-Colas et al. have measured the $\chi^{(3)}$ values for glasses elaborated within various ternary systems, namely TeO₂-Tl₂O-Bi₂O₃, TeO₂-Tl₂O-PbO and TeO₂- $Tl_2O-Ga_2O_3$ [39]. In particular, for the TeO_2-Tl_2O-PbO glasses, they measured $\chi^{(3)}$ values almost 10 times higher than those of SF59 glasses, justifying again the interest for such thallium tellurite-based chemical systems. Furthermore, for TeO₂-Tl₂O and TeO2-Tl2O-PbO glasses, Stegeman et al. have measured some Raman gain coefficients up to 50-60 times that of a 3.18 mm thick Corning 7980-2F fused silica sample [40]. In addition, we now briefly enumerate some examples of the literature where TeO2-ZnO-based glasses are doped with rare earth ions (e.g. Eu²⁺, Er³⁺, and Ho³⁺) for optical applications [4145]. The publications referenced [43–45] are extremely interesting, as they justify the use of tellurite glasses for rare earth doping, due to their low phonon energies (one of the lowest among oxide glasses). In particular, the luminescence and upconversion properties (like up-conversion efficiency) are detailed in those publications. As a last illustration, very recently, Jaba et al. reported the effects of the Er_2O_3 content on the local structure and on spectroscopic properties of Er^{3+} -doped zinc tellurite glasses [46].

As mentioned above, this list is far from being exhaustive but testifies already to the intense and diverse research activities in the field of TeO₂-based glasses. Finally, we would like now to end up this introduction by stating why we selected the TeO₂-TlO_{0.5}-ZnO ternary system as a matter of new investigations. First, some anterior work was carried out in our research group on optical poling of glasses elaborated within the TeO₂-ZnO or TeO₂-Tl₂O binary systems. Indeed, Vrillet et al. reported in [14] that SHG can be optically induced for such glasses. Furthermore, as stated in [39], $\chi^{(3)}$ values of thallium tellurite based glasses are among the highest values for tellurite glasses. It is therefore expected to also obtain high third order optical non-linearities, and to be able to generate a second harmonic, for glasses elaborated in the TeO₂-TlO_{0.5}-ZnO ternary system. Indeed, we suspect that Tl₂O will favour the hyperpolarisability ($\chi^{(3)}$) and that ZnO will increase the thermal stability and improve the optical damage threshold. Moreover, as indicated in Fig. 1, the glass forming domain limits for the binary systems are relatively extended. Thus, one expects the existence of a large glass forming domain in the case of the ternary system, allowing some simple and easy elaboration of pellets suitable for optical poling tests. All these combined reasons justify our selection.

Therefore, this work is mainly dedicated to report the feasibility to elaborate new glasses in the TeO_2-Tl_2O-ZnO ternary system, suitable for optical characterizations. In such chemical system, a large glass forming domain was evidenced. The thermal, as well as the structural characteristics of the glasses were determined. The influence of the thallium oxide content on the aforementioned characteristics was particularly investigated. This paper finally relates the possibility to generate a Second Harmonic, induced by optical poling, in those glasses. Second Harmonic Generation



Fig. 1. Glass forming domain within the TeO_2 - $TIO_{0.5}$ -ZnO ternary system. All the tested compositions lead to glass formation, except compositions labeled 1, 12 and 18, where crystalline phases are obtained. The dashed lines indicate the limits of the glass forming domains for TeO_2 - $TIO_{0.5}$ and TeO_2 -ZnO binary systems.

amplitude, as well as optical transmission data, was measured as a function of the thallium oxide content.

2. Experimental procedures

Glasses were prepared by melting intimately various quantities of TeO₂, Tl₂CO₃ and ZnO powders, in platinum crucibles, at 700 °C for 20 min. Tl₂CO₃ and ZnO were commercial products (Aldrich 99.9%) and TeO₂ was prepared from the decomposition at 550 °C, under air, of the H₆TeO₆ orthotelluric acid (Aldrich 99.9%). The melts were air-quenched into a brass ring, deposited over a preheated brass block, to obtain cylindrical samples 10 mm wide and 3 mm thick. The glass samples were then annealed 40 °C below their glass transition temperature for 10 h in order to release the thermal stresses resulting from the quenching. Both heating and cooling ramps were carefully fixed at a low value (2°/min). X-ray diffraction was used to verify the glassy state of the samples. At the limits of the glass forming domain, either α -TeO₂ or ZnTeO₃ compounds were evidenced.

The thermal characteristics (*i.e.* glass transition and onset crystallization temperatures) were determined with a commercial differential scanning calorimetry apparatus. All the calorimetric data measured for the various tested compositions are listed in Table 1.

The vibrational spectra of all the glasses were recorded in the 200–900 cm⁻¹ frequency range, with a micro-Raman spectrometer (Horiba-Jobin Yvon, T64000 model), equipped with a CCD detector and an Ar⁺ laser (514.5 nm line). Raman experiments are performed in a backscattering geometry, on powders resulting from the grinding of the tellurite glasses before laser exposure. The diameter of the laser spot focused at the sample was about 1 μ m. Measurements were carried out with a laser output power of 100 mW. The spectral resolution is about 4.5 cm⁻¹. We emphasize that, after the poling experiments, we briefly checked the irradiated areas: no particular sign of crystallization was evidenced.

Among the elaborated glasses, three of them were selected and then mechanically polished to obtain plane discs suitable for the optical characterizations. The corresponding chemical compositions of such glasses are the following: $(80 - x)TeO_2-xTIO_{0.5}-20ZnO$, where x is equal to 10, 20 and 30 mol%, respectively. The optical transmission measurements were carried out in the 300–

Table 1

Table summarizing all the information (chemical composition, crystallographic nature, calorimetric data) related to all the elaborated materials. $T_{\rm g}$, T_0 correspond respectively to the glass transition and to the first onset crystallization temperatures. Data highlighted in bold font correspond to a varying TlO_{0.5} content, while maintaining a fixed ZnO content.

Sample number	Chemical composition (mol%)		Specific temperatures (°C)			Sample nature	
	TeO ₂	TlO _{0.5}	ZnO	$T_{\rm g}$	T_0	$T_0 - T_g$	
1	80	10	10	x	x	x	α -TeO ₂
2	75	5	20	314	375	61	Amorphous
3	70	20	10	249	314	65	Amorphous
4	70	14	16	275	346	71	Amorphous
5	70	10	20	293	358	65	Amorphous
6	65	15	20	274	362	88	Amorphous
7	65	5	30	318	388	70	Amorphous
8	60	30	10	207	350	143	Amorphous
9	60	20	20	250	347	97	Amorphous
10	60	10	30	299	354	55	Amorphous
11	55	25	20	228	323	95	Amorphous
12	55	5	40	x	x	х	ZnTeO ₃
13	50	40	10	164	325	159	Amorphous
14	50	30	20	206	319	113	Amorphous
15	50	20	30	252	311	59	Amorphous
16	45	45	10	125	200	75	Amorphous
17	45	35	20	181	308	127	Amorphous
18	40	25	35	x	x	x	ZnTeO ₃



Fig. 2. Sketch of the experimental set up used to generate and then read the second order non-linearity. H: half-wave plates, L: lenses, F: filters, DC: doubling crystal, P: polarizer, PD: photodiode, D: diaphragm, PMT: photomultiplier tube, F1: 2 green blocking RG 850 filters, F2: 2 BG-18 colored glass filters (IR absorber), F3: 10 nm band pass interference filter centered at 532 nm.

2000 nm range, at normal incidence, with a Varian Cary 5000 spectrophotometer operated in dual beam mode.

The schematic representation of the experimental set-up used to induce and read the second order non-linearity is shown in Fig. 2. The light source was a pulsed Nd-YAG laser. It was operated at a repetition rate of 10 Hz and with a pulse width of 20 ns. The output beam was frequency doubled in a Potassium Titanyl Phosphate (KTP) crystal. The diameter of the laser beam at the focal point was measured with an infrared camera and was estimated to be about 60 µm. The ratio between fundamental (1064 nm) and SH (532 nm) lights was controlled by varying the laser beam energy and the phase matching condition of the KTP crystal with half-wave plates H1 and H2, respectively. In the writing phase, both fundamental and SH light were collinearly irradiating the sample, while in the reading phase two green blocking RG 850 filters (F1) were introduced in the beam path, so that only the fundamental light reached the sample. The SH light intensity generated by the sample was detected by a photomultiplier tube. Any residual fundamental light was absorbed by 2 BG-18 coloured glass filters (F2), which was followed by a 10 nm band pass interference filter centered at 532 nm (F3). The signal was measured on an oscilloscope, triggered by a photodiode.

Each poled area was systematically irradiated first by the fundamental wave (*i.e.* λ = 1064 nm) in order to verify that no SH signal was detected. In addition, we systematically paid extreme attention to discriminate in between true Second Harmonic Generation and green-fluorescence. Each glass was poled with the same $PPD_{\omega}/PPD_{2\omega}$ ratio between fundamental and SH lights (PPD stands for Peak Power Density). PPD₁₀₆₄ and PPD₅₃₂ poling values were measured with an energy meter or some photodiode, and are equal to 0.24 and 0.13 GW/cm², respectively. PPD_{1064} reading value is equal to 0.19 GW/cm². If PPDs were adjusted in order to avoid any laser damage of the glasses, the $PPD_{\omega}/PPD_{2\omega}$ ratio still remains to be adjusted in order to optimize the amplitude of SHG. As well, we point out that PPDs are approximately one order of magnitude lower than the ones reported in [14], suggesting very likely in our case (i.e. nanosecond pulses), that additional effects (mainly thermal effects) would play a role in the poling process (see discussion later). In addition, for each glass, we systematically recorded two sets of data collected from two different poled areas: the SHG intensities were then averaged. Finally, according to some theoretical background [47], as the amplitude of the second order non-linearity is proportional to the square of the thickness of the probed medium, the raw SHG data have thus been normalized to the square of each sample thickness. In our SHG measurements, we finally estimate the error bars to be about 10%. The error bars include the slight energy fluctuations of the laser that we noticed.

3. Results and discussion

Various chemical compositions have been tested in the TeO₂– TlO_{0.5}–ZnO system in the aim of elaborating samples (pellets) suitable for SHG experiments. The TeO₂–TlO_{0.5}–ZnO ternary diagram with all the tested compositions is displayed in Fig. 1. In addition, all the corresponding data are gathered in Table 1. Fig. 1 shows that a relatively large glass domain already exists, even if the glass domain limits have not been strictly established yet. Indeed, some compositions still remain to be explored, on the Tl-rich side of the ternary diagram. The aspect (color) of the glasses varies with the composition, from what looks like completely transparent (Zn-richer part) to yellowish (Tl-richer part) glasses.

All the calorimetric data are listed in Table 1. In particular, we wish to emphasize the strong effect of the Tl_2O modifier concentration on both T_g and T_0 values. Fig. 3a indicates the variation of both T_g and T_0 values versus the Tl_2O content, for a constant ZnO content. Both T_g and T_0 are reduced with the increase in the Tl_2O content; the former being more affected. Such variation of the glass transition temperature was already observed in the case of TeO_2 – Tl_2O binary glasses [31,32]. As a consequence, the $(T_0 - T_g)$ difference, which reflects the thermal stability of the glass, is increased as indicated in Fig. 3b. Such results constitute some interesting information in case of potential fiber-drawing applications.

According to Fig. 3c, when considering now a varying ZnO content, for a constant Tl₂O content, the glass transition temperature remains constant. However, for glasses elaborated within the binary TeO₂-ZnO system. Sekiva clearly showed that the ZnO addition leads to an increase in the glass transition temperature [48]. This evolution of $T_{\rm g}$ can then be understood if one considers, in the case of the TeO₂-TlO_{0.5}-ZnO ternary system, the effects of both Tl₂O and ZnO modifier concentrations simultaneously. In fact, while increasing the Tl₂O content for a constant ZnO concentration, the Tl/Te ratio directly increases (main contribution) and, at the same time, the ZnO/Te ratio indirectly increases (minor contribution). On the other hand, while increasing the ZnO content for a constant Tl₂O concentration, the Zn/Te ratio directly increases (main contribution) and, at the same time, the Tl/Te ratio indirectly increases (minor contribution). Therefore, the evolution of T_{g} represented in Fig. 3a can be mainly attributed to the Tl₂O addition, whereas the evolution of T_g showed in Fig. 3c could be explained by the two antagonistic effects of the addition of ZnO and Tl₂O oxide modifiers.

The vibrational properties of the elaborated glasses were studied with Raman spectroscopy. The evolution of the Raman spectra, as a function of the Tl_2O content, for a fixed ZnO concentration, and as a function of the ZnO content, for a fixed Tl_2O concentration, is displayed in Fig. 4a and b, respectively. As was discussed in [33], several bands can be clearly identified:

- a first one, located at roughly 660 cm⁻¹, corresponding to the symmetric stretching vibration of the equatorial Te–O bonds within the TeO₄ groups.
- a second one, located at roughly 740 cm⁻¹, corresponding to the symmetric synchronous vibration of the TeO₃^{2–} ortho-anions.
- a third one, located at roughly 445 cm⁻¹, corresponding to the bending deformation of the Te–O···Te bridges, mixed with the axial Te–O bond stretching.
- a fourth and weak one, located below 300 cm⁻¹, corresponding to the bending deformation of O–Te–O angles.

The data in Fig. 4a and b clearly indicate the relative intensity increase of the second band in respect to the first one, as a function of the addition of either Tl_2O or ZnO modifiers, respectively. This



Fig. 3. (a) Evolution of both T_g and T_0 versus the TlO_{0.5} content; (b) evolution of the $T_g - T_0$ difference versus the TlO_{0.5} content; (c) evolution of both T_g and T_0 versus the ZnO content. The dotted lines are present only as guides for the eyes.

intensity change corresponds to the transformation of TeO₄ disphenoids into $[TeO_3]^{2-}$ trigonal pyramid-like ortho-groups, which reflects the depolymerization of the glass. Such a modification of the TeO₂ glassy framework into island-type ortho-tellurite structures was already observed for both TeO₂– ZnO and TeO₂–Tl₂O binary systems, respectively [30–32], and thus occurs as well for the TeO₂–TlO_{0.5}–ZnO ternary system. The progressive decay of the band near 445 cm⁻¹ gives the real evidence for the disappearance of the TeO₂ framework which



Fig. 4. (a) Superimposition of the normalized Raman spectra for glasses presenting various $TIO_{0.5}$ contents, for a constant ZnO content: X labels the molar percentage in $TIO_{0.5}$. (b) Superimposition of the normalized Raman spectra for glasses presenting various ZnO contents, for a constant $TIO_{0.5}$ content: X labels the molar percentage in ZnO.

transforms into isolated TeO_3^{2-} units (see [33,34]). Such decay is more pronounced in Fig. 4a than in Fig. 4b, as the Tl/Te ratio varies from 0.067 to 0.6 (*i.e.* a variation of a factor of 10), whereas the Zn/ Te ratio varies from 0.14 to 0.6 (*i.e.* a variation of a factor of 4.2). Here, the effect of each oxide modifier concentration increase is identical, in the sense that it systematically leads to the depolymerization of the glass framework.

Three glasses were selected (see Section 2) in order to study the impact of the Tl₂O addition on the optical properties. The optical transmission data are represented in Fig. 5a, where a transmission level slightly below 80% in the near infrared range is noticed. In the 1500-2000 nm range (transparent region), each sample presents more or less the same optical transmission value, thus indicating that the refractive indices are very similar (see below). However, some discrepancies between the three glasses can be evidenced in the visible range: indeed, the 70TeO₂-10TlO_{0.5}-20ZnO glass seems to transmit less light than the two others (which behave similarly). The reason of this difference is so far unknown. For indication, the optical transmission values for the three glasses, measured at ω (1064 nm) and 2ω (532 nm), are listed in Table 2. In the insert of Fig. 5a, a magnification of the optical transmission in the 300-800 nm range is represented. The optical transmission of a α -TeO₂ single crystal is given as a reference in order to highlight the noticeable red-shift of the absorption/transmission threshold with the increase in the Tl₂O content of the glass. For each glass,



Fig. 5. (a) Optical transmission data for the (80 - x)TeO₂-xTIO_{0.5}-20ZnO glasses (with x = 10, 20 or 30 mol%), in the 300-2000 nm range. Insert: magnification of the 300-800 nm range in order to highlight the red-shift of the optical transmission/ absorption edge. The optical transmission of a α -TeO₂ single crystal is indicated as a matter of reference. (b) Absorption coefficient α (cm⁻¹) in the 350-800 nm range. The arrow points out the red-shift of the optical transmission/absorption edge.

we have derived the refractive index n from the optical transmission data, in the transparent region. In this region, the optical transmission coefficient T can be related to the refractive index by the formula:

$$T=\frac{2n}{n^2+1}$$

At 2 μ m, these values have been calculated and are reported in Table 2. The values obtained are perfectly compatible with what was reported by El-Mallawany in [2], for a huge variety of tellurite glasses, and in particular, for TeO₂–ZnO and TeO₂–Tl₂O binary glasses.

Finally, the approximate (reflections at the two glass-air interfaces are not taken into account) absorption coefficient α

Table 2

Optical transmission coefficient data at ω and 2ω , and refractive index at 2 μ m, for the three listed glasses.

Glass composition	Optical transmis coefficient T	Refractive index <i>n</i>		
	$T_{2\omega}$ (532 nm)	T_{ω} (1064 nm)	(at 2 µm)	
70TeO2-10TlO0.5-20ZnO	0.682	0.763	2.08	
60TeO ₂ -20TlO _{0.5} -20ZnO	0.739	0.790	2.05	
50TeO2-30TlO0.5-20ZnO	0.735	0.785	2.04	



Fig. 6. Normalized Second Harmonic Generation intensity versus time for the $(80 - x)\text{TeO}_2-x\text{TIO}_{0.5}-20\text{ZnO}$ glasses (with x = 10, 20 or 30 mol%). (a) During the poling process of the non-linearity, with PPD₁₀₆₄ = 0.24 GW/cm² and PPD₅₃₂ = 0.13 GW/cm². (b) During continuous reading process, after 10 min poling of the 60TeO₂-20TIO_{0.5}-20ZnO glass, with PPD₁₀₆₄ = 0.19 GW/cm². The dotted line is present only as a guide for the eyes.

was directly derived from the optical transmission data, using the following formula:

$$\alpha = -\frac{1}{d}\ln(T),$$

where *d* corresponds to the sample thickness, and α is expressed in cm⁻¹. Fig. 5b indicates the evolution of the absorption threshold as a function of the Tl₂O content. These data also clearly testify to the red-shift of the absorption/transmission threshold, reflecting that the optical band-gap is reduced with the increase in the Tl₂O content.

As mentioned in Section 1, previously in our laboratory, Vrillet et al. demonstrated the generation of a second harmonic signal in optically poled glasses elaborated in several binary systems, and in particular in the case of $TeO_2-TIO_{0.5}$ and TeO_2-ZnO systems [14]. In this present work, we unambiguously evidence the generation of a second order non-linearity optically created in those new $TeO_2-TIO_{0.5}-ZnO$ glasses. This is showed in Fig. 6, where the SHG intensity is displayed as a function of the poling and reading time, respectively. The poling curve (Fig. 6a) is typical for poling experiments. Indeed, the SHG amplitude saturates after a few minutes of exposure of the glasses: we consider that a poling time of 5–10 min is typically sufficient to saturate the SHG signal. We emphasize first that our experimental conditions to induce the poling process are different from those reported in [14], in the case of TeO_2-Tl_2O glasses. In our case, we have used nanosecond pulses (20 ns) with PDD of about 10 times lower than in [14], whereas they used picosecond pulses (80 ps). Therefore, in our experimental conditions, we cannot rule out thermal effects during the poling process, which was excluded in [14]. The first probable signature of the existence of thermal effects would be the fact that saturation of the SH signal is reached faster than in [14]. This will be discussed in more details below.

We cannot directly and strictly compare our data with the data reported in [14]. First, as explained immediately above, the temporal poling regimes are different. Then, the composition, and thus the structure, of the analyzed tellurite glasses are different. We are indeed working on ternary glasses whereas Vrillet et al. carried out SHG experiments on binary glasses. However, comparing these two sets of data still remains very interesting and, somehow, relevant. In addition, one has to admit that optical poling data available in the literature for similar tellurite systems are unfortunately limited to the results reported in [14], which are mainly focused on TeO₂–ZnO or TeO₂–Tl₂O binary glasses.

Our data indicate that the SHG amplitude seems to be increasing with the increasing Tl_2O content (Fig. 6a). However, Vrillet et al. previously noticed a reduction of the SHG amplitude with increasing Tl_2O content [14], thus, apparently, in contradiction with our observations.

Nevertheless, this observation/conclusion should be moderated in light of the above and following comments. First, our data concern lower Tl₂O content (in our case, from 10 to 30 mol%) than the ones discussed in [14], where the Tl₂O content varies from 25 to 50 mol%. Thus, one cannot immediately compare the two concentration ranges. As an argument, the SHG amplitude could, for instance, saturate for a Tl₂O concentration around 25-30 mol %, and decrease for higher Tl₂O contents. If one admits the latter assumption, our data are not in contradiction with the data published in [14]. Moreover, our data concern poled ternary glasses. Thus, the effect of the second modifier cation (*i.e.* Zn) must be taken into account in order to be rigorous. Vrillet et al. reported a strong increase in the SHG amplitude for poled TeO₂-ZnO glasses [14]. The amplitude was approximately multiplied by a factor of 10 for ZnO contents ranging from 20 up to 35 mol%, and then decreased for a ZnO content of 40 mol%. In our case, the ZnO content is fixed to 20 mol% but we have previously mentioned that the Zn/Te ratio indirectly increases, as Tl₂O is incorporated. In fact, the combined effects of both ZnO and Tl₂O modifiers could result in an increase of the SHG signal. Thus, it appears that the results extracted from [14] could become now compatible with our measurements.

Finally, our SHG data for poled TeO₂-Tl₂O-ZnO glasses should be compared to the non-linear optical properties of "similar" thallium tellurite glasses. The term "similar" should be understood in the sense that the second oxide modifier, ZnO, could be for instance replaced by PbO. The third order non-linear susceptibility $(\chi^{(3)})$ was measured, for TeO₂-Tl₂O-PbO glasses. The measurements revealed an increase of the $\chi^{(3)}$ value with the increase in the Tl₂O content, for various fixed PbO contents [39]. In particular, the $\chi^{(3)}$ value for the three glasses of the following compositions $(70TeO_2 - 10TlO_{0.5} - 20PbO, 64TeO_2 - 16TlO_{0.5} - 20PbO and 56TeO_2 - 10TlO_{0.5} - 10TLO_$ 24TlO_{0.5}-20PbO) was measured at 0.8 μ m, using a Mach-Zehnder interferometer. We selected intentionally such compositions as the PbO content is equal to 20 mol% (comparable to 20 mol% in ZnO). The respective $\chi^{(3)}$ values were obtained: 320, 433 and 567 $\times 10^{-23}$ m²/V². Interestingly, for similar Tl₂O contents, it can be noticed that the $\chi^{(2)}$ amplitude detected for our TeO₂-Tl₂O-ZnO poled glasses follows exactly the same trend as the $\chi^{(3)}$ value measured for TeO₂–Tl₂O–PbO glasses [39]. These results are then relatively similar as it is believed that $\chi^{(3)}$ is related to $\chi^{(2)}$ via the following relationship: $\chi^{(2)} = \chi^{(3)} \times E_{dc}$, where E_{dc} represents the internal electric field [49,50].

The SHG decay curve (Fig. 6b) is measured after a poling time of 10 min, for a unique glass of the following composition: 60TeO₂-20TlO_{0.5}-20ZnO. As stated earlier, we know after such poling time of 10 min (see Fig. 6a), that the SHG signal is saturated. Thus, assuming an exponential decay for the erasing of the SHG signal during the reading process, one obtains a time constant of about 37 min. Such value is approximately 6 times higher than the one reported in [14] in the case of a 70 mol% TeO₂-30 mol% ZnO glassy sample. Despite the difference in the chemical nature of the systems, we suspect that thermal effects play here the main role in order to explain why the SHG signal lasts for so long. Indeed, in our case, only slightly more than 60% of the SHG signal is lost after 40 min of continuous reading, whereas in [14], 75% of the SHG signal is lost after the same reading time. Such observation suggests more persistency of the SHG signal, after being poled with a pulsed nanosecond laser. However, as the chemical nature of the systems is different, at this stage of the study, it is impossible to draw any definite conclusion concerning laser dynamics effects on SHG.

4. Conclusion

We reported on the possibility to elaborate new glasses in the TeO_2 -TlO_{0.5}-ZnO ternary system. The glass forming domain for the elaboration of glassy pellets suitable for optical poling appears to be already large, even if it is not fully established yet. The impact of both Tl₂O and ZnO addition on both calorimetric and structural characteristics of the glasses was examined. The addition of each oxide modifier clearly provokes a depolymerization of the glass framework, as testified by the Raman spectroscopy data. Optical properties, such as transmission data, were measured as a function of the Tl₂O content, evidencing a red-shift of the absorption/ transmission threshold with the increase in the Tl₂O content; *i.e.* a reduction of the optical band-gap. Finally, in this work, we achieved our main goal, which was to prove the possibility to generate a second order non-linearity in those new TeO₂-Tl₂O-ZnO glasses. For the tested compositions, Second Harmonic Generation was unambiguously detected after optical poling, with a tendency for the SHG amplitude to be amplified by the Tl₂O addition. Work will be now focused on the study of the laser dynamics (nanosecond or picosecond regime) on both the poling efficiency and the SHG persistency. Work will be also to scrutinize the poled regions using Raman spectroscopy in order to thoroughly search for any potential structural changes of the glass after laser exposure.

Acknowledgements

This work was carried out within the frame of the national project REGLIS. Some of the authors would like to thank as well the Région Limousin for its financial support.

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