

Influence of Hydroxyl Group on IR Transparency of Tellurite-Based Glasses

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A study of the glass properties with two opposite levels of hydroxyl content is presented for two different tellurite glass families with molar composition $70\text{TeO}_2\text{-}10\text{Bi}_2\text{O}_3\text{-}20\text{ZnO}$ and $80\text{TeO}_2\text{-}20\text{Nb}_2\text{O}_5$. We show that melting tellurite-based glasses in a dried-oxidant atmosphere (relative humidity <1%) reduces drastically the OH impurities. The effect of reducing the OH content on the glass properties such as characteristic temperatures, crystallization stability (ΔT), density, and microhardness is investigated.

Introduction

Tellurite-based (TeO_2) oxide glasses have been identified as promising materials for optical applications such as Raman gain or supercontinuum generation,^{1,2} due to their high linear and nonlinear optical properties, good thermal stability, low melting temperatures, and a wide transparency range from 0.4 to 5 μm .³ TeO_2 -based glasses possess among the highest optical nonlinearity of vitreous oxide materials, but to form a glassy state, TeO_2 has to be mixed with other elements. Thus, glass modifiers have to be well-chosen, to not lead to an adverse decrease in the nonlinear optical properties. The introduction of a glass modifier with d^0 electronic configuration (e.g., Ti^{4+} , Nb^{5+} , W^{6+}) or ions with a lone pair electron (e.g., Tl^+ , Pb^{2+} , Bi^{3+})⁴ allows glasses to maintain high nonlinear optical behavior.^{5,6} For many optical applications, optical fibers are desired. This target requires the development of high purity materials exhibiting limited or no absorption in the transmission bandwidth in the near infrared (NIR). Hydroxyl groups are among the impurities which can dramatically decrease transmission in the near infrared (NIR) window. Indeed, in tellurite glasses, impurities such as hydroxyl groups are common and exhibit a strong absorption in the spectral range around 3 μm with harmonics at around 1.4 and 1 μm .^{7,8}

In this study, the synthesis of two different glass systems, $\text{TeO}_2\text{-Nb}_2\text{O}_5$ and $\text{TeO}_2\text{-Bi}_2\text{O}_3\text{-ZnO}$, is analyzed, with the intent of quantifying the impact of the glass' OH content on the evolution of optical, physical, and chemical properties. In the literature, few works have been conducted on the identification of the hydroxyl group in tellurite glass. Thanks to IR absorption spectroscopy, a comparative study is proposed between the orthotelluric acid, $\text{Te}(\text{OH})_6$, and the studied glasses. Calculation using density functional theory has been applied to reinforce the assignment of the absorption features in the infrared.

Experimental Procedures

Tellurite-based glasses in the investigated host systems $\text{TeO}_2\text{-Nb}_2\text{O}_5$ and $\text{TeO}_2\text{-Bi}_2\text{O}_3\text{-ZnO}$ were

prepared in 10 g batches via a standard melt quench method.⁹ The glasses were prepared from commercial raw compounds (TeO_2 99.99% [Alfa Aesar], Nb_2O_5 99.9985% [Alfa Aesar], ZnO 99.0% [Alfa Aesar], and Bi_2O_3 99.9995% [Alfa Aesar]). To compare the influence of the melting atmosphere on the resulting OH content, glasses of the same composition were weighed, batched, and melted outside and inside a air-dried purged glove box (relative humidity <1%). Before melting, raw materials were preheated at 200, 300, and 400°C to eliminate organic components or bound surface impurities such as water, hydroxyl, and carbonyl groups. The batch mixtures were melted in a platinum crucible at 800°C, for 15 min. The glasses were then quenched on a preheated brass plate and annealed overnight at a temperature 40°C below their respective glass transition temperatures (T_g). Glass elemental compositions were checked by energy dispersive X-ray spectroscopy (EDS), and their vitreous nature was confirmed by X-ray diffraction (XRD).

The absorption spectra of the glass samples were recorded at room temperature; UV-Vis-NIR absorption spectra were recorded using a dual beam UV-Vis-NIR Perkin Elmer Lambda 900 spectrophotometer on 1.5-mm-thick, optically polished samples. Absorbance in the infrared region was measured using a Magna-IR 560 Fourier transformed infrared spectrometer (FTIR) from Nicolet. The system was purged with N_2 to remove atmospheric water and CO_2 in the sample chamber prior to measurement. The amount of hydroxyl content present in the glass network can be approximated by $N_{\text{OH}} = N_A/L\epsilon \ln(1/T)$, where N_A is the Avogadro constant ($6.022 \times 10^{23}/\text{mol}$), L the sample thickness (cm), T the transmittance, and ϵ the absorption coefficient of the OH entity using reference data from silica glass ($49 \times 10^3 \text{ cm}^2/\text{mol}$) extrapolated for tellurite glasses.¹⁰

The geometry optimization of orthotelluric acid was calculated using the Gaussian 09 program (1) at the density functional theory level using the CAM-B3LYP functional, which is the hybrid B3LYP function corrected by the coulomb attenuation method to better account for long distance forces. The used basis set for the O and H atoms was the Gaussian Pople base

6-311 + +G** with polarization functions¹¹ and diffuse functions (+), and the LanL2DZ basis for the Te atom. The vibrational spectra were calculated in the harmonic approximation. For comparison with experiment, the calculated intensities were converted to Lorentzian bands with half-width of 7/cm, and the vibrational frequencies were multiplied by the 0.96 factor in the 0–2000/cm range and by the 0.91 factor in the 2000–4000/cm range (for OH contributions), taking into account the anharmonic effect.

Raman spectra were obtained using a Senterra (Bruker Optik) micro-Raman system employing a 785 nm excitation with 10 mW incident power at the sample. Confirmation that this analysis did not change the glass structure was obtained by repeating the analysis on the same spot twice for each measurement.

Characteristic temperatures such as the glass transition temperature (T_g), the onset of crystallization (T_x), and the crystallization temperature (T_p) were determined by differential scanning calorimetry (DSC) at a heating rate of 10°C/min from room temperature to 550°C using a commercial DSC apparatus (Seiko Instruments Inc.). The measurements were carried out in a hermetically sealed aluminum pan. The density of the bulk glass materials was measured by Archimedes principle using diethylphtalate as the immersion liquid; the accuracy of this technique is better than 0.02 g/cm³. The Vickers microhardness H_v of investigated glasses was measured using a Shimadzu DUH-211S Microhardness tester, with a static load of 100 mN generating an accuracy of $\pm 3\%$.

Results and Discussion

The main impurities in tellurite-based glasses leading to major optical loss in the near- to mid-infrared (MIR) spectral region are hydroxyl groups. The high frequency range [4000–1500/cm] IR transmission spectra of the two tellurite glasses (80TeO₂-20Nb₂O₅ and 70TeO₂-10Bi₂O₃-20ZnO) melted in air or under a controlled dried atmosphere (approximately 1% relative humidity at room temperature) are reported in Figures 1 and 2. This spectral range spans the fundamental and harmonic regions of the hydroxyl absorptions. Note that both IR spectra for the glasses prepared in ambient air show two broadbands centered near 3000 and 2250/cm and a sharp, low frequency edge below 1700/cm. In contrast, for the glasses melted in a glove

box under dry conditions, these two absorption bands decrease drastically, while the sharp band edge below 1700/cm remains unchanged.

Bands at 3000 and 2250/cm are clearly correlated with the presence of OH in the glass structure. The last bands at 1700/cm is assigned to the multiphonon vibration edge characteristic of the glass network. In germanotellurite glasses, Feng *et al.*¹² assigned the band at 3000/cm to weakly hydrogen-bonded OH, and the band at 2250/cm to a very strong hydrogen-bonded OH mode, according to previous works on silicates.¹³

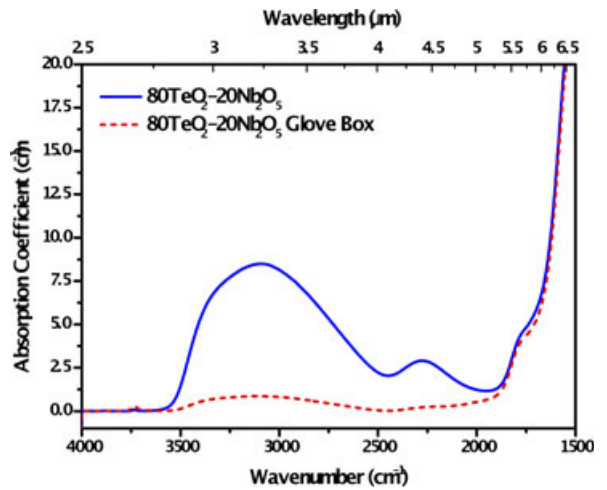


Fig. 1. Comparison of IR spectra of 80TeO₂-20Nb₂O₅ glass with melting environment.

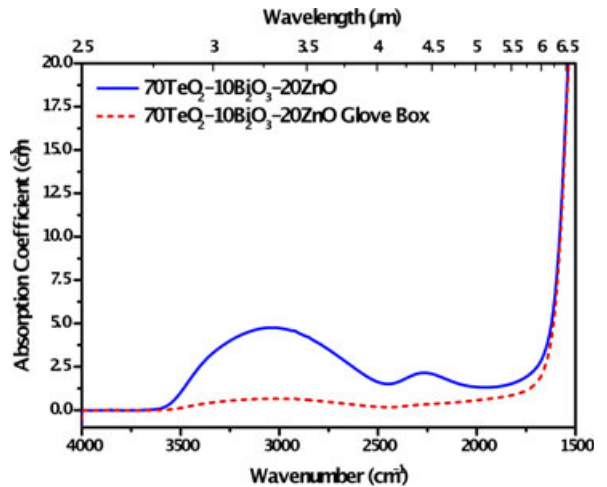


Fig. 2. Comparison of IR spectra of 70TeO₂-10Bi₂O₃-20ZnO glass with melting environment.

We disagree with the nature of the band at 2250/cm, the attribution to strong hydrogen-bonded OH makes sense in silica glasses but cannot be directly extrapolated to tellurite glass network. In term of molecular arrangement, the silica and tellurite glass networks are different and do not have the same reactivity within atmosphere. We propose to highlight this opposition with numerical and experimental models.

Regarding the signature of hydroxyl species in tellurite-based materials, the IR absorption spectrum of orthotelluric acid $\text{Te}(\text{OH})_6$, shown in Figure 3, illustrates relevant spectroscopic information, which clarifies Te–OH peak assignments. The calculated IR spectrum of orthotelluric acid, made using the crystal structure parameters proposed by Mullica *et al.*,¹⁴ is also reported in Figure 3 for comparison with the experimentally measured spectra. The calculated IR spectrum gives OH contributions (from the isolated $\text{Te}(\text{OH})_6$ moiety) in the high frequency range, that is, for stretching modes ν_{OH} at 3400/cm and bending modes δ_{OH} at 1000/cm. The calculated contributions below 1000/cm are due to the coordinated tellurite entities.¹⁵ The experimental IR spectrum of orthotelluric acid seems to be consistent with the calculated one, but a few remarks must be pointed out. First, we observe a strong broadening of the bands in the high frequency part of the spectrum, which is indeed indicative of a broad distribution of $\text{Te}(\text{OH})_6$ moieties that interact quite strongly through hydrogen bonding with neighboring moieties, and most likely with a few external molecules of bound water, because of the strong hydrophilic

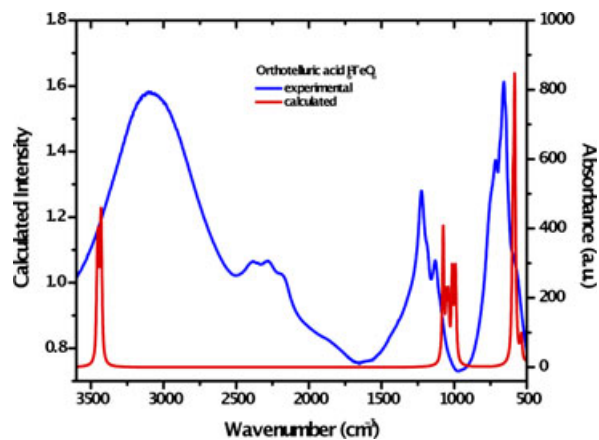


Fig. 3. Measured and calculated IR spectra of orthotelluric acid $\text{Te}(\text{OH})_6$.

nature of that acid. As a consequence of this large set of interactions, the stretching and bending characters of normal modes of hydroxyl groups mix together and the resulting stretching modes ν_{OH} softens close to 3000/cm while the bending modes δ_{OH} harden at 1100–1200/cm. Following the same trends, the internal stretching modes involving Te–O bonds hardens to approximately 700/cm. However, in the harmonic approximation, no calculated contribution is expected in the range 2000–2500/cm. We assign the medium broadband observed at 2250/cm to an anharmonic contribution of the bending mode at $2\delta_{\text{OH}}$ (approximately 2250/cm) because of the strong interaction of the medium (glass). Clearly, this additional band is correlated with the presence of hydroxyl species (Figs. 1 and 2), which are known to be anharmonic oscillators. It is thus expected that a condensation of the network occurs when the content of hydroxyl decreases and new Te–O–Te bonds form to result in interconnected TeO_6 octahedral.¹⁶ One can notice a shift in frequency between the calculated and experimental spectra. The molecular environment is not taken into account in the calculation and is at the origin of a high and low frequencies coupling.

Fusion during melting and quenching has an important influence on the OH content in tellurite glass. The band cross-section at 3000/cm (3.3 μm) for 80 TeO_2 -20 Nb_2O_5 reduces from around 8.5/cm to 0.9/cm (a reduction of 89%) with purification, while it decreases from 4.8/cm to 0.7/cm (85% reduction) for the 70 TeO_2 -10 Bi_2O_3 -20 ZnO glass composition. Note that the two glasses examined have similarly high mol fractions (80 and 70 mol%) of tellurium oxide, the most hygroscopic of the batch constituents. The strong reduction in the 80 TeO_2 -20 Nb_2O_5 glass composition has to be related to the higher level of hydroxyl content in the higher TeO_2 -containing base glass as compared to the 70 TeO_2 -10 Bi_2O_3 -20 ZnO glass composition. This OH reduction represents a good step but can still be improved; hydroxyl content is significantly higher compared with other tellurite glasses present in the literature.^{17,18}

Figures 4 and 5 illustrate a focus on the low frequency range [1000–150/cm] of the glass' Raman spectrum, which is indicative of the glass network. For that purpose, the Raman spectra of the tellurite glasses 80 TeO_2 -20 Nb_2O_5 and 70 TeO_2 -10 Bi_2O_3 -20 ZnO , elaborated in air and under a controlled dried atmosphere, are shown. As can be observed, the peak Raman

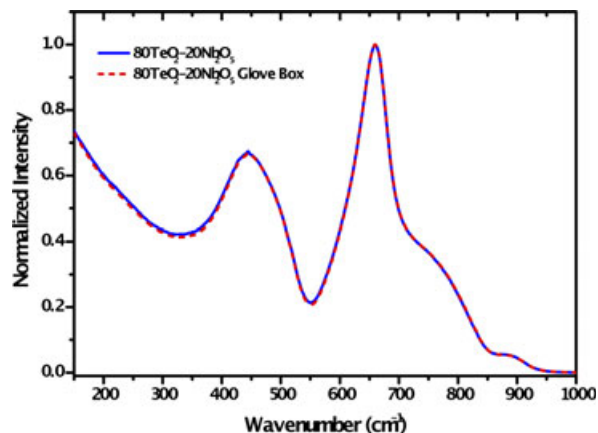


Fig. 4. Normalized Raman spectrum of the $80\text{TeO}_2\text{-}20\text{Nb}_2\text{O}_5$ glass (normalized to 760cm^{-1}).

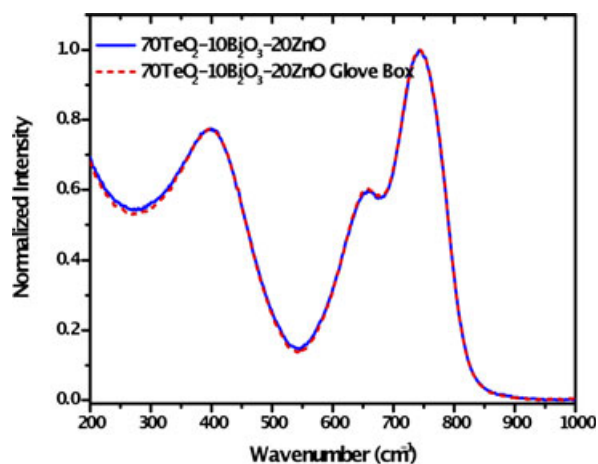


Fig. 5. Raman spectrum of the $70\text{TeO}_2\text{-}10\text{Bi}_2\text{O}_3\text{-}20\text{ZnO}$ glass (normalized to 760cm^{-1}).

intensities are dominated primarily by the tellurite oxide contributions, firstly, as it is the most preponderant compound in the glass network, and secondly, as it exhibits the strongest polarizability compared with the weaker τ spectral signatures of Nb_2O_5 , Bi_2O_3 , or ZnO .⁹ When cation modifiers are introduced within the TeO_2 matrix, structural variations are interpreted by a progressive transformation of TeO_4 trigonal bipyramidal (tbp) units into TeO_3 trigonal pyramidal (tp) units, via the intermediate bonding state TeO_{3+1} . TeO_{3+1} corresponds to a distorted TeO_4 entity with one long Te-O bond, as found in TeO_2 crystals and some binary tellurite crystals.¹⁹ The vibrational modes

observed in our study can be associated with the following different structural elements:

- Starting from the low frequency range, the band at 380cm^{-1} is assigned to symmetric stretching anion motion of Bi-O-Bi in the $[\text{BiO}_6]$ octahedral units.^{20,21}
- The band at $400\text{--}450\text{cm}^{-1}$ results from highly coupled bending and stretching modes of continuous chains Te-O-Te of corner sharing TeO_4 , TeO_{3+1} , and TeO_3 polyhedral.
- Bands located at 610 and 660cm^{-1} (mainly Raman active) originate, respectively, from anti-symmetric and symmetric stretching of TeO_4 units forming a continuous network.
- The high energy broad shoulder ($720\text{--}830\text{cm}^{-1}$) is expected to contain at least two main contributions currently assigned to stretching modes of TeO_{3+1} and TeO_3 units,
- Finally, NbO_6 vibrational contributions are also expected at 890cm^{-1} .

Note that the reduction in OH content has no significant influence on that range of the Raman spectrum, in agreement with results previously reported by Massera *et al.*²² due to an initial low OH content.

The influence of OH on glass properties in a low OH content glasses [$50\text{--}800$ ppm] has been looked by Arriagada *et al.* and Karmakar *et al.* in phosphate glass matrices, and observed that hydroxyl content in glass can have a profound effect on its properties, and especially on the thermal and physical properties, with a proportional dependence of the glass transition temperature, the density, and the refractive index with the low OH content. The impact of OH has been investigated on the thermal and physical properties, in the tellurite glasses and summarized in Table I.

For both glasses, the UV cut-off edge is identical, and no difference exists between as-prepared and dried glasses indicating no clear influence of the hydroxyl species in this spectral region. The tellurite (Te-O) network (backbone) contribution is believed to define the position of the UV absorption edge.

Karmakar *et al.*²³ reported a densification of the glass structure during the reduction in hydroxyl content in phosphate glasses, from 2.63 g/cm^3 with 770 ppm of OH to 2.76 g/cm^3 with 60 ppm of OH. In our case, such an effect is not observed; the change of OH content in the glass network does not appear to affect the glass density values, which are all within the error bars of the measurement.

Table I. Evolution of Characteristic Temperatures, Glass Stability, Volumetric Weight, Microhardness, Cut-Off Energy, and Hydroxyl Content in 80TeO₂-20Nb₂O₅ and 70TeO₂-10Bi₂O₃-20ZnO Glass Compositions, Melted or Not in an Air-Dried Glove Box

Glass composition	T_g [$\pm 2^\circ\text{C}$]	T_x [$\pm 2^\circ\text{C}$]	T_p [$\pm 2^\circ\text{C}$]	ΔT	ρ (g/cm ³) [± 0.02]	H_v (kg/mm ²) [$\pm 3\%$]	Cut-off energy (eV)	OH (10 ¹⁹ ions/cm ³) [± 0.01 ions/cm ³]
80TeO ₂ -20Nb ₂ O ₅	340	445	458	105	5.49	320	3.22	6.13 (315 ppm)
80TeO ₂ -20Nb ₂ O ₅ Glove box	344	450	467	106	5.48	333	3.22	0.66 (34 ppm)
70TeO ₂ -10Bi ₂ O ₃ -20ZnO	340	444	460	104	6.21	294	3.06	7.18 (326 ppm)
70TeO ₂ -10Bi ₂ O ₃ -20ZnO Glove box	344	450	468	106	6.20	305	3.06	1.58 (72 ppm)

Karmakar *et al.* have shown that the hydroxyl content can have a dramatic effect on the thermal and physical properties of metaphosphate glass, with a proportional dependence with OH content on the glass transition temperatures from $T_g = 490^\circ\text{C}$ (OH content picked at 770 ppm) to $T_g = 565^\circ\text{C}$ (OH content picked at 60 ppm). This dependence of glass transition temperature T_g on the OH content reflects the structural changes and has been observed for high OH-containing glasses, compared with our tellurite glasses. From this study, we demonstrate that melting and quenching in a glove box with air-dried atmosphere represents a desirable protocol to reduce the OH content, as it does not change the glass composition nor the glass' characteristic thermal properties. Closely examining the thermal properties summarized in Table 1, it can be seen that our measurements show that the reduction in OH content does not significantly affect the glass transition temperature T_g for both glass systems, and within the error bars of $\pm 2^\circ\text{C}$. Concerning the dry glasses, an increase in the onset crystallization temperature is barely observed for both glass compositions, suggesting that the presence of OH groups is affecting the inhomogeneous crystallization kinetics by a probable weakening of the glass network. This is consistent with data shown for the glass' mechanical properties as illustrated by the measured Vickers hardness data. Our results show a higher hardness for both dried glasses, with measured hardness values well (approximately 4%), above the error. We thus confirm that the decrease in OH content increases the average bonding energy of the network system. Thus, a purified, dry material is slightly more mechanically robust than a

material synthesized in ambient air atmosphere with no particular precaution. Such an effect can be associated with a lower degree of polymerization of the network due to the increase in nonbridging oxygen atoms, which act as charge defects that may strongly interact with water from the environment to produce hydroxyl groups OH⁻ anion.²⁴ Such species have also been linked to a reduction in crystallization stability as these M-OH bonds are weak links where crystallization may occur. This argument is substantiated in this data, as the removal of moisture serves to enhance (increase) ΔT .

Conclusion

In this article, we have proposed to look at the evolution of the glass properties from an unpurified to purified material using a glass melting process into a dried-air atmosphere. It has been performed on two different tellurite glass matrices, TeO₂-Nb₂O₅ and TeO₂-Bi₂O₃-ZnO. We have demonstrated via IR spectroscopy that a melt prepared in a dried-air atmosphere containing less than 1% humidity permits to reduce mid-infrared optical losses attributable to OH content. Our study showed a reduction of 89% and 85% of the IR absorption of the ν_{OH} stretching modes at 3.3 μm in TeO₂-Nb₂O₅ and TeO₂-Bi₂O₃-ZnO glass networks, respectively. This decrease in OH content does not significantly modify the macroscopic characteristics of the glass (glass transition temperature, density, and cut-off energy) and its microscopic glass structure. We have also observed a small improvement in crystallization

tendency (increase in ΔT) and increase in the key crystallization temperatures, as well as microhardness with the reduction in the OH impurity content. These results show that melting and quenching tellurite glasses in dried-air atmosphere can clearly constitute a viable route to obtain purified materials with enhanced optical and mechanical properties. Such attributes are critical for the production of high-quality tellurite optical fibers.

Acknowledgments

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