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# Raman structural investigation of manganese doped tellurite glasses

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The influence of a gradual addition of the modifier manganese oxide on the structure of tellurite glass, containing borate oxide and a very litle amount of strontium floride, has been studied. The Raman spectra of $xMnO\cdot(1-x)[70TeO_2\cdot25B_2O_3\cdot5SrF_2]$ with $0 \le x \le 0.5$ are characterized by three main bands, located around 450, 670 and 770 $cm^{-1}$. At lower content of manganese oxide ($x \le 0.03$) the $TeO_4$ units dominate the glass network. At high content of manganese oxide ($x > 0.03$) the glass network is predominantly formed from $TeO_3$ units. While the modifier is added, the ratio of $TeO_4/TeO_3$ structural units is change. Therefore, the addition of manganese oxide determines the transformation of $TeO_4$ trigonal bipyramides to $TeO_3$ trigonal pyramids. The gradual addition of the MnO on the glass structure involves a change in the coordination number of tellurite atoms from 4 to 3.

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*Keywords:* Tellurite glasses, Structure, Raman spectroscopy

## 1. Introduction

Non-crystalline solid tellurite glasses continue to intrigue both academic and industry researchers not only because of their many technical applications, but also because of a fundamental interest in understanding their microscopic mechanisms. Tellurite glasses present scientific importance due to their pronounced nonlinear optical properties as well to their potential as an appropriate material for fiber amplifier. Furthermore, tellurite glasses have high refractive indices in the range from 1.85 to 2.2 and show good infrared transmittance [1]. Tellurite glasses are of current interest in technology, as components of optically nonlinear materials, and fundamentally, due to the unusual glass forming properties of tellurium dioxide ($TeO_2$). In this oxide tellurium is four-coordinated but nevertheless only a conditional glass former; addition of other oxides gives rise to ranges of excellent glass formation. The optical properties arise from the polarizable lone pair of electrons carried by each tellurium atom [2]. Understanding the structure of these glasses and its relation to their properties is important in their use.

Raman spectroscopy is an effective tool for resolving the structure of local arrangements in glasses. Raman spectra are particularly well suited for studying boro-tellurite glasses because peaks in the region of 600 to 800 $cm^{-1}$ are generally attributed only to tellurite and not to the borate species, which by comparison, scatter weakly.

Glasses having the compositions $xMnO\cdot(1-x)[70TeO_2\cdot25B_2O_3\cdot5SrF_2]$ with $0 \le x \le 0.5$ were studied by means of Raman spectroscopy. The influence of a gradual addition of the modifier manganese oxide on the glass structure is studied in this paper.

## 2. Experimental

The glasses were prepared by the conventional melt quench-ing method. The starting materials $H_3BO_3$, $TeO_2$, $SrF_2$ and $MnCO_3$ were mixed thoroughly by grinding in appropriate quantities so as to constitute a 5 g batch. The ground mixtures were melted in sintered corundum crucibles at 1200 K in an electric furnace. The mixtures were put into the electric furnace direct at this temperature. After 30 minute the batches were quenched between stainless steel plates kept at room temperature.

For the Raman spectra the 514.5 nm line of an Ar-ion laser (Spectra -Physics Model 2016) was used. The plasma lines were avoided by means of a filter prism (Anaspek) and the laser beam was focused on the sample with an Olympus microscope objective (Olympus ULWD 80, NA 0.75). The back-scattered light was collected by the same objective and then was focused on the entrance slit of the detection system. A Dilor-XY Raman triple monochromator with a Peltier cooled, intensified diode array with 1024 diodes is employed as the light detection system. The back-scattering configuration allows the observation of the sample surface before light exposure. The laser power was 100 mW. The measurements were carried out at room temperature. The spectral data are processed using Dilor hardware and specially developed software. The spectra were recorded with a resolution of 2 $cm^{-1}$ and the spectral data were analyzed with Origin software.

## 3. Results

Raman spectra of $xMnO\cdot(1-x)[70TeO_2\cdot25B_2O_3\cdot5SrF_2]$ glasses with various content of manganese oxide ($0 \le x \le 0.5$) were recorded.

The Raman spectra of the composition $xMnO\cdot(1-x)[70TeO_2\cdot25B_2O_3\cdot5SrF_2]$ with $0 \leq x \leq 0.5$ are characterized by three main bands, located around 450 $cm^{-1}$, 670 $cm^{-1}$, and 770 $cm^{-1}$. At low content of MnO ($x \leq 0.03$) the ~450 $cm^{-1}$ band is the dominant band in the corresponding spectrum. In same range the intensity of ~670 $cm^{-1}$ band is higher than the intensity of ~770 $cm^{-1}$ band. For $x > 0.03$ the ~450 $cm^{-1}$ band decreases in intensity and the ~670 $cm^{-1}$ band becomes smaller than the ~770 $cm^{-1}$ band. The ~450 $cm^{-1}$ Raman band disappears at high content of manganese oxide ($x > 0.3$) and the 670 $cm^{-1}$ band is present like a week shoulder. At this concentration of manganese oxide the Raman spectrum is clearly dominated by a single Raman band located at 770 $cm^{-1}$.

## 4. Discussion

Crystalline α-$TeO_2$ (paratellurite) is tetragonal [3]. Early work suggested the network in tellurite glasses consisted of strongly deformed [$TeO_4$] units, analogous in structure to rhombic β-$TeO_2$ (tellurite), where $Te^{+4}$ is coordinated to four oxygen atoms. However, later work proved that in tellurite minerals and glasses, a number of polyhedra are formed, tellurium atoms having the coordination: 3, 3+1 and 4. In glasses this variety of coordination is due to the presence of network modifiers and intermediates [3, 4].

*Table 1. Coordination of tellurite glasses and both forms of crystalline $TeO_2$: paratellurite (α-$TeO_2$) and tellurite (β-$TeO_2$) [5].*

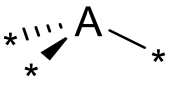
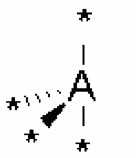
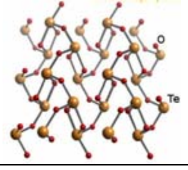
| | Coordination | Structure | Te-O bond distance/nm | Te-O-Te bond angle/° |
|---|---|---|---|---|
| Crystal | 3 | Trigonal pyramid<br><br>$TeO_3$ (tp) | 0.195 | 95 |
| Crystal | 4 | Trigonal bipyramid<br><br>$TeO_4$ (tbp) | 0.200 | 120±20 (equatorial)<br>180±30 (axial) |
| Glass | 3, 4, 3+1 | tp and tbp<br> | 0.209 (equatorial)<br>0.191 (axial) | 92,1±6,6 (equatorial)<br>162.6 (axial) |

Table 1 summarizes the two extreme cases of coordination in both forms of crystalline $TeO_2$: α-$TeO_2$ and β-$TeO_2$ and coordination in tellurite glasses. Recent work on the structure of tellurite glasses has concluded that the network more closely resembles paratellurite (α-$TeO_2$), where [$TeO_4$] units are only linked at their corners [5]. Combining $TeO_2$ with other glass forming (such as $B_2O_3$), network modifiers (such as MnO) and intermediates (such as $SrF_2$) results in structural modification to chain like structures.

The main structural units present in the structure of tellurite glasses are $TeO_4$ trigonal bipyramids (tbp), $TeO_3$ trigonal pyramids (tp) and $TeO_{3+1}$ polyhedra [6], as shown in Fig 1. In the $TeO_4$ trigonal bipyramids unit a lone pair of electrons occupies an equatorial site of the Te $sp^3d$ orbital whereas in $TeO_3$ trigonal pyramids the lone pair of electrons occupies the apex of the Te $sp^3$ orbital [7]. The concentration of these structural units is strongly affected by the glass composition. Therefore, the type and the concentration of network modifying oxide alter the structure of the glass.

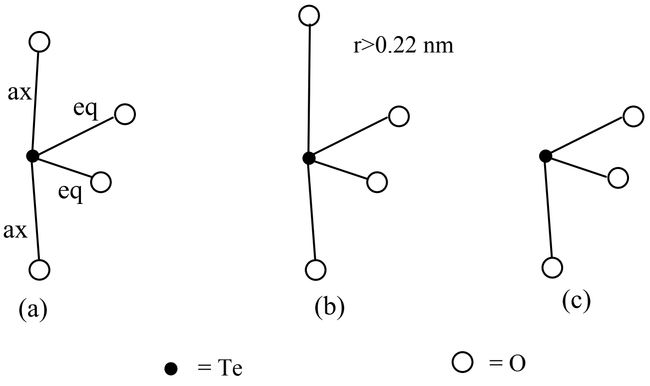


*Fig. 1. Structural units in tellurite glasses: a) $TeO_4$ trigonal bipyramide (tbp), b) $TeO_{3+1}$ polyhedra, c) $TeO_3$ trigonal pyramid (tp).*

The Raman spectra of $xMnO\cdot(1-x)[70TeO_2\cdot25B_2O_3\cdot5SrF_2]$ are characterized by three bands, located around ~450 $cm^{-1}$, ~670 $cm^{-1}$, and ~770 $cm^{-1}$ as shown Fig 2. These bands also appear in the Raman spectrum of α-$TeO_2$ glass [6, 8]. The bands centered around 450 $cm^{-1}$ and 670 $cm^{-1}$ have been assigned to the symmetric and antisymmetric vibration of Te-O-Te linkages in $TeO_4$ trigonal bipyramids (tellurium atom is four coordinated). The 770 $cm^{-1}$ band was attributed to the stretching vibration between tellurium and nonbridging oxygen atoms from $TeO_3$ trigonal pyramids (tellurium atom is three coordinated), or from intermediate $TeO_{3+1}$ polyhedra [8]. The ~770 $cm^{-1}$ Raman band can be also assigned to the symmetric breathing vibration of six membered rings with one $BO_4$ tetrahedron (i.e. triborate, tetraborate, or pentaborate) [9]. Because, the peaks from the region of 600 to 800 $cm^{-1}$ are attributed generally only to tellurite and not to the borate groups which, by comparison, scatter weakly, we can not argue what type of borate groups are present in the structure of investigated glasses.

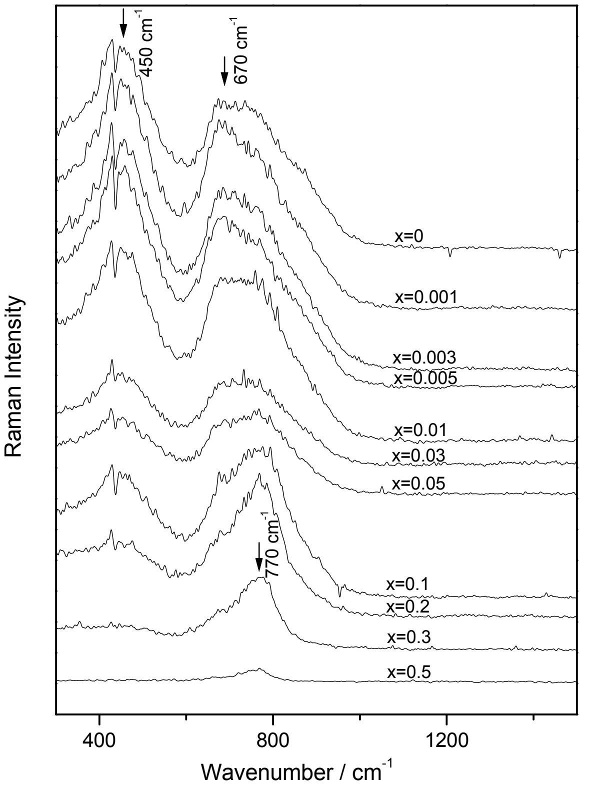


*Fig. 2. Raman Spectra of* $xMnO\cdot(1-x)[70TeO_2\cdot25B_2O_3\cdot5SrF_2]$ *glasses with* $0 \leq x \leq 0.5$.

The Raman spectrum of boro-tellurite glass without manganese oxide indicates a structure formed by trigonal bipyramids and trigonal pyramids units. Because the intensities of 450 $cm^{-1}$ and 670 $cm^{-1}$ bands are higher than the intensity of 770 $cm^{-1}$ band, we conclude that the number of trigonal bipyramids is higher than the number of trigonal pyramids in the glass network. Thus, the ratio of $TeO_4/TeO_3$ structural units is greater than one.

In Raman spectra of these glasses, a very week shoulder appears at ~ 800 $cm^{-1}$ due to boroxol ring oxygen breathing, involving a very little boron motion (boron atom coordination is three) [9].

The Raman spectra of studied glasses changes significantly with the modification of the MnO content.

At low content of MnO ($0 \leq x \leq 0.03$) the ~450 $cm^{-1}$ band is the dominant band. In the same range of concentration the intensity of ~670 $cm^{-1}$ band is higher than the intensity of ~770 $cm^{-1}$ band. At low content of manganese oxide the structure of the glass doesn't change significantly. There are both trigonal bipyramids and trigonal pyramids units, and the ratio of $TeO_4/TeO_3$ structural units decreases but remains greater than one.

For $x > 0.03$ the ~450 $cm^{-1}$ band decreases in intensity and the ~670 $cm^{-1}$ band becomes smaller than the ~770 $cm^{-1}$ band. Therefore, we conclude that the manganese oxide start to change to the structure of the glass. In this range of concentration, there are still both trigonal bipyramids and trigonal pyramids units, but the ratio of $TeO_4/TeO_3$ structural units changed and became smaller than one. The addition of the MnO determines a change of the tellurium coordination from four to three. The number of trigonal bipyramids is smaller than the number of trigonal pyramids in the glass network.

The ~450 $cm^{-1}$ Raman band almost disappears at high content of manganese oxide ($x>0.3$) and the 670 $cm^{-1}$ band is present like a week shoulder. At this concentration of manganese oxide the Raman spectrum is clear dominated by a single band, the 770 $cm^{-1}$ Raman band. Thus, at high content of manganese ions the glass structure contains mostly trigonal pyramids and tellurium ions are three fold coordinated. High content of manganese oxide determines disappearance of almost all trigonal bipyramids units from the glass network by changing the tellurium coordination.

Therefore, the addition of manganese oxide determines the transformation of $TeO_4$ trigonal bipyramides in $TeO_3$ trigonal pyramids.

## 5. Conclusions

The structure of boro-tellurite glass without manganese oxide is formed from trigonal bipyramids ($TeO_4$) and trigonal pyramids ($TeO_3$) units. The ratio of $TeO_4/TeO_3$ structural units is greater than one.

At low content of MnO ($0 \leq x \leq 0.03$) the structure of the glass doesn't change significantly. There are both trigonal bipyramids and trigonal pyramids units, and the ratio of $TeO_4/TeO_3$ structural units decreases, but remains greater than one.

At high content of manganese oxide ($x > 0.03$) the glass structure begins to change. The ratio of $TeO_4/TeO_3$ structural units became smaller than one. The tellurium coordination changed from four to three. The number of trigonal bipyramids is smaller than the number of trigonal pyramids in the glass network.

At very high content of manganese oxide ($x > 0.3$) the glass structure is dominated by trigonal pyramids, and tellurium ions are three fold coordinated. High content of manganese oxide determines disappearance of almost all trigonal bipyramids units from the glass network by changing the tellurium coordination. At very high content of manganese oxide the glass network is predominantly formed from $TeO_3$ units.

Therefore, the addition of manganese oxide determines the transformation of $TeO_4$ trigonal bipyramids in $TeO_3$ trigonal pyramids. The gradual addition of the MnO on the glass structure involves the change in the coordination number of tellurium atoms from 4 to 3. The ratio of $TeO_4$/$TeO_3$ structural units changes with the modifier addition.

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