Tracking of Formed Crystalline Phases in the Binary Silver Tellurite Glass-ceramics

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Abstract

Glasses and glass-ceramics based on silver tellurite system xAg2O-(100-x)TeO2 (0 ≤ x ≤ 60 mol%) were prepared by melt-quenching method. The structure of the studied glasses and glass-ceramics was investigated by several techniques. XRD patterns reveal the existence of only one glassy region at 20 < x ≤ 30 mol% with two crystalline α-TeO2 and Ag2TeO3 phases that formed separately in the prepared samples below 20 and beyond 30 mol% Ag2O, respectively. The peaks intensity corresponding to the crystalline α-TeO2 and Ag2TeO3 phases was found to decrease and increase with Ag2O content, respectively. This may be correlated with changes in the concentration of Qn4 and Qn0 units that, respectively, build up the crystalline α-TeO2 and Ag2TeO3 phases. In the glassy region, there is no crystalline phase, which may be attributed to the abundance of the deformed Qn4 units that build up the glassy phase, and the concentrations of Qn4 and Qn0 units are neglected in this region. SEM and TEM micrographs and the related electron diffraction patterns (EDP) confirmed the formation of crystallized clusters in Ag2O-rich glasses.

Keywords: Ag2O-TeO2 glasses and glass-ceramics; Ag2O-rich TeO2; Qn4 units; Clusters; Ag2TeO3 phase; α-TeO2 phase; XRD; TEM and EDP techniques.

1. Introduction

Tellurite glasses are characterized by their desirable physical properties. They have wide glass formation regions [1–5], extremely high refractive index, high dielectric constant, excellent infrared transmittance, and low melting temperature [6–9]. In addition, TeO2 is considered as a good agent for crystallization [10].

The structure of tellurite glasses has attracted considerable attention. Various investigators used infrared [2,8,19–22,11–18], Raman [2,15,19,23–25], nuclear magnetic resonance spectroscopies [3,6,26,27] and neutron diffraction [28–31] to study the structural properties of tellurite glasses. Tellurite network is composed of bridging Q4 (TeO4) and deformed Q3 (TeO3+) units below 20 mol% alkali oxide. While in the range 20-30 mol% of alkali oxide Q5 (TeO5) were existed with (n=1& 0) having higher non-bridging oxygen atoms (NBOs) in tellurite network and increasing as alkali content increased. The isolated Q0 (TeO3–) along with Q1 (Te2O52–) structural units are the main formed species at 50 mol% of alkali oxide.

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Most of previous studies have focused on the structural species in the modified tellurite in the glassy region for most alkali tellurite glasses [15,26,28,31–33]. Studies on Ag$_2$O-TeO$_2$ glasses are so far limited to be considered [34,35]. Therefore, this work is aimed to shed more light on the structural features of Ag$_2$O-TeO$_2$ glasses and glass-ceramics and to identify the crystallized phases that formed within the Ag$_2$O-TeO$_2$ glass-ceramics.

2. Experimental Methods

Samples with nominal composition $x$Ag$_2$O-(100-$x$)TeO$_2$ (0 ≤ $x$ ≤ 60 mol%) were prepared by mixing of AgNO$_3$ and TeO$_2$, in porcelain crucibles. The crucible was firstly transferred into the electric furnace and kept at 300°C for 30 minutes and then it was heated for 10 minutes at a temperature ranged between 800 and 900 °C depending on the composition. Finally, the melt was poured and rapidly quenched at room temperature.

The crystallized phases were identified by the (XRD) technique using PANalytical X’Pert PRO XRD system using a Cu Kα target with secondary monochromator (λ = 1.540 Å). The tube operated at 45 kV- 40 mA. Measurements were made over the range 10° to 70° on 2θ scale. The measurements were carried out at Nano Technology and Advanced Materials Central Lab (NAMCL), Research Institute, Cairo University.

The morphology of the Ag$_2$O-TeO$_2$ glasses and glass-ceramics (bulk-fractured surface) was examined using a Scanning Electron Microscope (SEM), model JEOL–JSM–6510LV attached with energy dispersive spectroscopy (EDS) unit, model Oxford–X–Max 20. The size of the formed structural units is examined by Transmission Electron Microscope (TEM), model JEOL JEM-2100 with an electron acceleration voltage of 200 kV. Structural information could be obtained by using electron diffraction patterns (EDP). The measurements were made at the Spectroscopy Unit, Faculty of Science, Mansoura University.

3. Results and Discussion

Local structure of Ag$_2$O-TeO$_2$ glasses

Under normal conditions, tellurium oxide cannot form a glass without a modifier [28,36,37]. In both crystalline and amorphous tellurium oxide, the Q$_4^4$ units are considered as the basic dominant structural units that build the network of the material [22,23,26]. In this case, the tellurium atom is surrounded by four bridging oxygen atoms (BOs). Two BOs are located in axial vertices and the others are in the equatorial positions. In addition, one lone pair of electrons is occupied in a third equatorial site as presented in Fig (1) [2,23].

![Fig. 1: The tellurium (IV)–oxygen polyhedra found in alkali tellurite crystals and glasses.](image)

The tellurium polyhedral units can be represented by Q$_m^n$ notation, where (n) is the number of bridging oxygens (BOs) and (m) is the coordination number of the Te atom [38]. It was reported that, the addition of a modifier and/or intermediate oxides into tellurite glasses results in changing Q$_m^n$ unit toward formation of non-bridging oxygen ions (NBOs). These changes are presented schematically in Fig (1).
The mechanism of occurred changes in $Q_m^n$ units that plotted in Fig (1) are explained as following:

1- Firstly, below 10 mol% of modifier oxide such as (Li$_2$O, Ag$_2$O, etc.), it is entirely consumed to convert $Q_4^4$ to $Q_3^1$ via $Q_4^3$ units, because the later units are unstable and automatically transformed to ($Q_3^1$) once [23].

2- Beyond 10 mol% of modifier oxide, it is used to produce either $Q_3^1$ or $Q_3^0$ units depending on modifier oxide content [23].

3.1. X-ray diffraction:
XRD patterns of Ag$_2$O-TeO$_2$ glasses and glass-ceramics are shown in Figs. (2-a) and (2-b).

![X-ray diffraction pattern](image)

Fig. 2a: X-Ray diffraction pattern for $x$Ag$_2$O-(100-$x$)TeO$_2$ glasses and glass-ceramics; (0 ≤ $x$ ≤ 30 ) mol % Ag$_2$O containing tellurite glass and glass-ceramics respectively. Numbers at the plots refer to the concentration of Ag$_2$O (mol %).
Fig. 2b: X-Ray diffraction pattern for \(x\text{Ag}_2\text{O}-(100-x)\text{TeO}_2\) glasses and glass-ceramics; \((33 \leq x \leq 60)\) mol % \(\text{Ag}_2\text{O}\) containing tellurite glass and glass-ceramics respectively. Numbers at the plots refer to the concentration of \(\text{Ag}_2\text{O}\) (mol %).

The pattern of fused \(\text{TeO}_2\) shows many sharp peaks in the region \(\sim 22-66^\circ\). These peaks are related to \(\alpha\)-TeO\(_2\) crystalline phase (card number 78-1713C). The decrease in intensity of these peaks reflects a decrease in concentration of the \(Q^4_4\) units. This might be accompanied by an increase in the concentration of \(Q^1_3\) and/or \(Q^0_3\) units. The sharp peaks formed in the composition region \(0 < x \leq 20\) mol\% closely match those related to paratellurite (\(\alpha\)-TeO\(_2\)) (card number 78-1713C) which is built up by sharing corners of \(Q^4_4\) units. The intensity of these sharp peaks decreases with increasing \(\text{Ag}_2\text{O}\) content which reveals that there is an increase in the disorder of the glass matrix. These sharp peaks disappear completely between 22.5 and 30 mol\% \(\text{Ag}_2\text{O}\), while a broad hump arises at 30 mol\% \(\text{Ag}_2\text{O}\) revealing the completely amorphous nature of this composition. In this region the glassy state becomes dominant. Starting from the sample containing 33 mol\% \(\text{Ag}_2\text{O}\), a new sharp peaks-corresponding to \(\text{Ag}_2\text{TeO}_3\) crystalline phase (card number 83-1779 C) appears with maximum intensity at 50 mol\% \(\text{Ag}_2\text{O}\), where the structure becomes saturated with Ag\(^+\) ions. Beyond 50 mol\% \(\text{Ag}_2\text{O}\), additional small peaks (+) appeared which related to the metallic silver (card number 87-07117).

Changes in the XRD spectral features (intensity and angular position) can be explained on the basis of the following concepts:

1- \(\text{TeO}_2\) can be considered as a stable glass former by the effect of the addition of even small quantity of modifiers [39,40].

2- The glass forming ability of tellurium was found to increase with increasing the modifier content up to certain value (30 mol %).
3- For more than 30 mol% of modifier oxide, the glass forming ability is suppressed by forming a new crystalline Ag$_2$TeO$_3$ phase which consists of Q$^0_3$ units. The concentration of the latter increases with increasing modifier content at the expense of TeO$_2$ [32,39,40].

4- Maximum intensity of the peak related to crystallized Ag$_2$TeO$_3$ appears at 50 mol% when R=1, where R is the ratio (Ag$_2$O/TeO$_2$), as shown in Fig (2-b). The decrease in the intensity of peaks related to Ag$_2$TeO$_3$ for R>1 might be due to the decrease in the TeO$_2$ content. The presence of excess Ag$_2$O in such glass-ceramics may be considered as a reason for formation of metallic silver clusters.

Glasses enriched with both Ag$_2$O and the deshielded Q$^n_3$ units (where n= 0 & 1) have increasing ability toward formation of Ag$_2$TeO$_3$ crystalline phase and clusters of metallic Ag. This consideration is further supported by the appearance of new sharp diffraction peaks at 2θ = 31.2, 36.68, 51.84, 52.8, 61.76 and 62.52 degree in prepared samples containing 33–60 mol% Ag$_2$O. The presence of new diffraction peaks at 2θ =38.08 and 44.32 degree at high Ag$_2$O content (52.5, 55 & 60 mol %) might reflect the inability of the glass matrix to accommodate more of Ag$^+$ ions. As a result, these excess ions are forced to accumulate in these glasses forming atomic silver clusters. Similar structural changes were assumed by some authors [41,42] in fluorotellurite glasses.

3.2. SEM and EDS techniques

To explore the morphology of the Ag$_2$O–TeO$_2$ glasses and glass-ceramics, investigations were performed using SEM. SEM and EDS results agree well with that obtained by the XRD patterns and confirm it. The SEM micrograph of the as-prepared samples of (10, 25, 30, 35 and 50) mol% Ag$_2$O are shown in Figures 3(a, b, c, d, e & f), respectively. The electron micrographs of the samples with 50 and 55 mol% Ag$_2$O are shown in Figures 4(a & b) respectively. It is shown that the particle size increases with increasing Ag$_2$O content in the studied glasses. A. E. Ersundu et.al [43], have used SEM spectroscopy to study the microstructure of binary CdO-TeO$_2$, WO$_3$-TeO$_2$ and ternary CdO-WO$_3$-TeO$_3$ glasses before and after thermal treatment, it was concluded that the dark colored crystallites are due to α-TeO$_2$ for all glass compositions, while the white colored are rich with WO$_3$ and CdO and corresponding phases [43]. Figure (3-a) shows an interconnected columns or rods on the surface of the sample with 10 mol% Ag$_2$O, which corresponds to α-TeO$_2$ phase as induced from the XRD pattern in Fig. (1-a). These rods are assumed to be due to the α-TeO$_2$ phase and the background base may represent glassy Ag$_2$O–TeO$_2$ matrix. El Agamy et al. [41,42] proposed like these results in the NaF-TeO$_2$ and PbF$_2$-TeO$_2$ glasses and glass-ceramics. The micrograph of the samples containing 25 and 30 mol% Ag$_2$O are shown in Figs. 3(b & c), respectively. It shows white colored particles with different size dispersed separately through the base matrix. The base matrix is attributed to the modified glassy phase, while the white colored particles are corresponding to Ag$_2$TeO$_3$ crystalline phase. (Figs. 3c) shows that the particles in sample of 30 mol% Ag$_2$O are larger and denser than that of 25 mol%. SEM micrograph of the sample containing 35 mol% Ag$_2$O is shown in Figs. 3(d& e). Figure (3d) depicts cubic particles having different sizes start growing with fine-grain particles observed on the surface of sample with 30 mol% Ag$_2$O. Both of fine and cubic-particles might be correspond to Ag$_2$TeO$_3$ phase. Figure (3f) depicts formation of columns on the surface of the prepared 50 mol% Ag$_2$O sample. The cubic particles (Fig. 3d) that produced from fine-grains can be ascribed to the initial stage of the observed rods in the sample containing 50 mol% Ag$_2$O.
The rods have a larger size than that of cubic, revealing to a more ordering (Fig. 2a). The rods might be ascribed to Ag$_2$OTeO$_3$ phase as deduced from XRD pattern in Fig. (2-b). The micrograph of 50 mol% Ag$_2$O (Fig.4a) shows white-colored particles dispersed in the base matrix. These particles are corresponding to metallic Ag. Figure (4b) shows flowers-like crystallites in the prepared 55Ag$_2$O-45TeO$_2$ sample.

These flowers seem to be formed as a result of coalescence of white-particles in the sample of 50 mol% Ag$_2$O. These white flower-like crystallites are corresponding to metallic Ag as deduced from the XRD results.
SEM micrographs reveal a slight increase in particle size when increasing Ag₂O content from 25 to 30 mol% Ag₂O. It becomes clearer when forming the cubic and rods in samples of 35 and 50 % Ag₂O, respectively. It is proposed that, the particle-size is proportional to Ag₂O content. The fine-particles in samples 25 and 30 mol% Ag₂O represent the initial stage of the cubic shape formation, and the latter represents the first stage of rods growth. The glassy phase is predominant in the range 25 ≤ Ag₂O ≤ 30 mol%. Whereas, Ag₂TeO₃ phase appears with relatively low intensity at 33 mol% Ag₂O and grows with Ag₂O content until reaching maximum intensity at 50 mol% Ag₂O as in Fig. (2-b), which may be attributed to the formation of the rods respectively as seen in Figs. 3(e-f). So it can be concluded that, development of Ag₂TeO₃ phase within the prepared glass-ceramics can be done by increasing Ag₂O up to 50 mol% Ag₂O, where the structure becomes saturated with Ag₂TeO₃ phase and excess added of Ag₂O is precipitated inside the network as metallic silver as shown in Figs. (2-b) and (4-b).

EDS spectra of Ag₂O –TeO₂ glasses and glass-ceramics containing 10, 30, 50 and 55 mol% of Ag₂O are shown in Fig. 5. At 10, 30 mol % of Ag₂O, the increase in peak intensity of silver compared to that of Te with Ag₂O content supports the XRD results. The intensity of the Ag peak may refer to concentration of Ag⁺ ions in these NBOs units. However, at higher concentrations (≥ 50 mol% Ag₂O), the structure may become saturated with NBOs units containing Ag⁺ ions and the excess of Ag₂O is precipitated as metallic silver.

![Fig. 5: EDS spectrum of the xAg₂O.(100-x)TeO₂ glasses and glass-ceramics, x=10, 30, 50 and 55 mol% Ag₂O.](image)

3.3. TEM and EDP Techniques
The TEM and EDP results agree with those obtained by the SEM, EDS and XRD for selected samples. The TEM micrographs and electron diffraction pattern (EDP) for samples with 10, 30, 35 and 50 mol%
Ag₂O are shown in Fig. 6 (a, b, c& d) respectively. The TEM micrograph of 10 mol% Ag₂O sample shows rods along with fine-grains of (2-3) nm in size (Fig 6a).
The EDP pattern shows more ordering structure as shown in (Fig. 6a). For the sample with 30 mol% Ag$_2$O, the size of the formed particles was found to vary from 11 to 50 nm and the distribution of these particles in the network is randomly as presented in Fig. 6b. The diffused circles in the EDP patterns are characteristic of the amorphous matrix at Ag$_2$O = 30 mol% that mainly might be Ag$_2$O –TeO$_2$ phase. The TEM micrograph of the sample with 35 mol% Ag$_2$O shows that, these fine-particles are aggregated in large size (black zones) through the network (Fig.
4. Conclusions
The samples from xAg2O-(100-x)TeO2 (0 ≤ x ≤ 60 mol%) system were prepared and investigated through, XRD, SEM, EDS and TEM techniques. There are two mainly crystalline phases, α-TeO2 and Ag2TeO3. However, the crystallinity decreases with the Ag2O content below 20 mol% and disappears completely in the range (20< Ag2O ≤30) mol%, it returns to increase with the Ag2O content beyond 30 mol%. Q4 and Q5 units that, respectively, built up crystalline α-TeO2 and Ag2TeO3 phases are decreased and increased with addition of Ag2O below and beyond 30 mol% Ag2O, respectively. Disappearing of the formed crystalline phases in the glassy region might be due to abundance of the deformed Q3 units, related to the glassy phase, and the concentrations of both Q4 and Q5 units are neglected.

5. References
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