Effect of WO$_3$ on the glass transition and crystallization kinetics of borotellurite glasses

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Tellurite glasses of the system $x$WO$_3$–75TeO$_2$–(25–$x$)B$_2$O$_3$ (0≤$x$≤25 mol. %) were prepared and studied by differential thermal analysis to explore the effect of WO$_3$ on their glass transition and crystallization kinetics. The crystallization kinetics was studied under non-isothermal conditions using the formal theory of transformations for heterogeneous nucleation. The crystallization results were analyzed and both the activation energy of the crystallization process and the crystallization mechanism characterized. The phases into which the glass crystallizes were identified by X-ray diffraction. Diffractograms of the transformed material indicate the presence of microcrystallites of $\alpha$-tellurite, Te$_{0.95}$W$_{0.05}$O$_{2.05}$, Te$_2$W and B$_2$O$_3$ in the amorphous matrix.

Keywords: tellurite glass; crystallization kinetics; differential thermal analysis

1. Introduction

Academic and scientific studies of tellurite-based glasses have been the subject of many articles due to their interesting optical, electrical and magnetic properties. Their large nonlinear optical susceptibility and nonlinear refractive indices show that they have promising applications in nonlinear optical devices based on optical switching, optical memory, etc. [1–4]. Many investigations have been reported on the technological importance of tellurite glasses containing transitional metal ions (TMI) or rare earth ions in use as elements in memory switching devices and cathode materials for batteries [5–8]. TeO$_2$-based glasses show electrical conductivity several orders of magnitude higher than silicate, borate, and phosphate glasses containing the same amount and type of modifiers [9,10].

The structure of tellurite glasses has been investigated previously using IR, Raman spectroscopy, X-ray and neutron diffraction techniques. The main focus of these studies was on the structural units in the glass network. In general, the structure and the properties of oxide glasses are dependent strongly on the nature and the

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concentration of the constituent oxides. Thus, in tellurite glasses, modifier atoms cause changes in the basic structural units, namely TeO$_4$ trigonal bipyramid (tbp) and TeO$_3$ trigonal pyramid (tp) units, both of which have a lone pair of electrons occupying one of the equatorial positions [1–2,9]. Thus, the aforementioned properties of borotellurite glasses and the possibility for its management by change of the composition, as well as the structural changes prompted by this change, explain the interest towards the borotellurite glasses [11–15].

Based on the aforementioned aspects, the manufacture of tellurite glass ceramics or thermally stable tellurite glasses requires extensive studies on the crystallization kinetics in tellurite glasses by using valuable techniques such as differential thermal analysis (DTA) or differential scanning calorimetry (DSC) techniques. The study of crystallization kinetics using these techniques in many glass systems, especially tellurite-based glasses, has been widely discussed in the literature [16–23]. In addition, different methods associated with specific theoretical models have been proposed to study and calculate the crystallization kinetics from the exothermic peaks of the DTA curves under non-isothermal conditions [24–31]. Thus, this kind of investigation aims to shorten the path from the investigation to the application. In the present work, the effect of addition of WO$_3$ on the glass transition and crystallization kinetics of $x$WO$_3$–75TeO$_2$–(25–$x$)B$_2$O$_3$ ($x=0, 5, 10, 15, 20$, and 25 mol. %) glasses was studied using DTA with continuous heating of the sample at various uniform heating rates. The compositional dependence of the characteristic temperatures (glass transition temperature, $T_g$, the onset peak of crystallization, $T_c$, and the temperature peak of crystallization, $T_p$), the activation energy for the glass transition ($E_g$), the activation energy for crystallization ($E_c$) and the crystallization mechanism (Avrami exponent) is discussed. Finally, the crystalline phases corresponding to the crystallization process were identified by X-ray diffraction (XRD) measurements.

2. Experimental details

Glass samples with the formula $x$WO$_3$–75TeO$_2$–(25–$x$)B$_2$O$_3$, ($0 \leq x \leq 25$ mol. %) were prepared by the melt-quenching technique. Required quantities of Analar grade TeO$_2$, WO$_3$ and H$_3$BO$_3$ were mixed by grinding the mixture repeatedly to obtain a fine powder. The powder mix was melted in a covered platinum crucible in an electrically heated furnace under ordinary atmospheric conditions at a temperature of 1173 K for 2 h to homogenize the melt. Glasses in frits form were produced by quenching of glass melts in air. The non-crystalline nature of the prepared glasses was confirmed by X-ray diffraction using a Philips X-ray diffractometer PW/1710 with Ni-filtered Cu K$_\alpha$ radiation ($\lambda=1.542$ Å) operating at 40 kV and 30 mA. The patterns (not shown) revealed broad humps characteristic of the amorphous materials and did not reveal discrete or any sharp peaks.

The calorimetric measurements were carried out using a differential thermal analyzer (Shimadzu 50) with an accuracy of ±0.1 K. The instrument was calibrated for each heating rate. The glass powders (after being crushed into powder form) weighing 20 mg were contained in an aluminum crucible and the reference material was $\alpha$-alumina powder. The samples were heated in air at uniform heating rates
(α = 2.5, 5, 10, 15, 20 and 30 K/min). The values of the characteristic temperatures (T_g, T_c, and T_p) were determined with an accuracy of ±1 K.

3. Theoretical background

The theoretical bases of interpreting DTA data is provided by the formula theory of transformation kinetics that reports the crystallized volume fraction (χ) in time (t), using the Johnson–Mehl–Avrami equation [32]

\[ \chi = 1 - \exp(-kt)^n, \]

(1)

where n is an integer or half integer that depends on the mechanism of growth and the dimensionality of the crystal and k is defined as the effective (overall) reaction rate, which is usually assumed to have an Arrhenian temperature dependence \[ k = k_0 \exp(-E/RT) \], where E is the effective activation energy describing the overall crystallization process.

In a non-isothermal DTA experiment, the rate constant, K, changes continually with time due to the change of the temperature, and Equation (1) can be rewritten in the form [33]

\[ \chi(t) = 1 - \exp\left[ -\left( \int_0^t K[T(t)]dt \right)^n \right] = 1 - \exp(-I^n). \]

(2)

Then it is easy to derive the following equations as well, as detailed elsewhere [16,18]:

\[ \ln(T_p^2/\alpha) = -E_c/RT_p - \ln(K_0R/E), \]

(3)

where T_p is the temperature peak of crystallization and E_c is the activation energy of crystallization;

\[ \chi_p = n(0.37\alpha E_c)/(RT_p^2). \]

(4)

The kinetic exponent n can be calculated by using Equation (4). Then it is easy to deduce the dimensionality of crystal growth, m, through the following equation [33,34]:

\[ \left[ \frac{d\chi}{dT} \right]_p = mE\alpha(1 - \chi_p)/RT_p^2. \]

(5)

Equation (6) (see Section 4.1) was deduced by taking a sufficiently limited range of temperature (such as the range of crystallization peaks in DSC or DTA experiments) so that the fraction, 1/T^2, can be considered practically constant, and designating it with the subscript, p, the magnitudes corresponding to the maximum crystallization rate. For studying the crystallization kinetics of glasses when the nuclei formed during the heating at constant rate, α, are dominant, the kinetic exponent, n, is equal to m + 1 and when nuclei formed during any previous heat treatment prior to thermal analysis are dominant, n is equal to m. n is the Avrami parameter and m is the dimensionality of crystal growth [35,36].
4. Results and discussion

Before discussing the present results, it is worth shedding light on the binary system TeO₂–B₂O₃. According to studies of the macro liquid phase separation, this system consists of two layers: a transparent one, rich in TeO₂ and the other reasonably opaque, and rich in B₂O₃. Bürgler et al. [14] reported that an invariant point corresponding to a composition with 73.6 (mol. %) TeO₂ was found; from its location the system could be treated as a composite of two quite different regions. Uniformly distributed droplet-like heterogeneities are observed in both regions. Also, the phase determination in this system showed that the binary system is a simple eutectic, without formation of any compounds. A wide region of the stable miscibility gap has been determined. Another feature of this system is the existence of BO₃ groups, BO₄ tetrahedra and TeO₄ groups [37–41]. Increasing the WO₃ content will give rise to the appearance of WO₄ and WO₆ structural units, which has a pronounced effect up to 30 mol. % of WO₃ [9,42–44].

Accordingly, in this study, Figure 1 shows the DTA thermograms for the xWO₃–75TeO₂–(25 – x)B₂O₃ (0 ≤ x ≤ 25 mol. %) glasses recorded at a heating rate α = 15 K/min.

Figure 1. Typical DTA traces of xWO₃–75TeO₂–(25 – x)B₂O₃ (0 ≤ x ≤ 25 mol. %) glasses at a heating rate α = 15 K/min.
4.1. Glass transition

Determination of the so-called activation energy of enthalpy relaxation of the glass transition, or activation energy for the glass transition $E_G$, can be achieved by using the Kissinger formula, which was originally derived for the crystallization process.
but is suggested as being valid for the glass transition [16,45]. Therefore, Equation (3) can be rewritten in the following form:

\[ \ln \left( \frac{T_g^2}{\alpha} \right) = \frac{E_g}{R} + const., \]

where \( R \) is the universal gas constant. Values of \( E_g \) can be estimated from the \( \ln(T_g^2/\alpha) \) versus \( 1/T_g \) relation for different WO\(_3\) contents. The subscript \( g \) denotes the magnitude of values corresponding to the glass transition temperature. Figure 4 shows verification of the linearity of the above relation for the studied glasses. The obtained values of the glass transition activation energy, \( E_g \), are listed in Table 1. The increase in \( T_g \), and hence \( E_g \), with the increase in WO\(_3\) content may be attributed to the increase in the packing density, the dissociation energy, and the average force constant of the studied glasses, as observed elsewhere [9]. Another reason for the increase in \( T_g \), and hence \( E_g \), is that the coordination number of WO\(_3\) is 6 compared with B\(_2\)O\(_3\), which has a coordination number of 3; also, the bond strength of W–O is larger than that of B–O [46,47]. Thus, the increase in WO\(_3\) content will increase the cross-link density, which reflects an increase in the rigidity of the glass.

4.2. Crystallization kinetics

To evaluate the activation energy for crystallization, \( E_c \), the variation of \( T_p \) with \( \alpha \), according to Equation (4) [19,48], was used. From the experimental data, a plot of
ln(T_r^2/α) versus 1/T_r was obtained (Figure 5) for different compositions and Figure 6 shows the same plot for the second exothermic peak.

The activation energy (E_a) and the frequency factor (K_0) are then evaluated by least-squares fitting of Equation (3). The indices 1 and 2 in E_c1, E_c2, K_01 and K_02 denote the first and second peaks, respectively. Values of the activation energy of crystallization obtained for the two peaks are tabulated in Table 1. It is evident that, the activation energy for crystallization of the two crystallization peaks increases with the increase in the WO_3 content. El-Mallawany [1] reported that in tungsten tellurite glasses most of W^{6+} and Te^{4+} cations may join in the network structure, but a proportion may be located outside the glass network. These cations outside of the
Figure 5. Experimental plots of (a) $\ln(T_{p1}^2/\alpha)$ vs. $1000/T_{p1}$ for the first crystallization peak and (b) straight regression lines for $x\text{WO}_3 - 75\text{TeO}_2 - (25-x)\text{B}_2\text{O}_3$ ($0 \leq x \leq 25$ mol. %) glass system ($\alpha$ in K s$^{-1}$).

Figure 6. Plots of $\ln(T_p^2/\alpha)$ vs. $1000/T_p$ for the analyzed materials.
network structure, especially $W^{6+}$, may induce crystallization of tungsten oxide. Also, the increase in the hyperpolarizability of W–O bonds and their concentration, besides the $d$ orbital contribution, may increase both $T_p$ and $E_c$.

The ratio between the ordinates of the DSC curve and the total area of a peak gives the corresponding crystallization rates, which makes it possible to build the curves for the exothermic peaks depicted in Figure 7 for the 75TeO$_2$–5WO$_3$–20B$_2$O$_3$ glass as an example. It is found that the values of $(d\chi/dt)_p$ increase with an increase in the heating rate [36,49]. From the experimental values of the $(d\chi/dt)_p$ one can calculate the kinetic exponents $n$ and $m$ by using Equations (4) and (5). The mean values, $\langle n \rangle$ and $\langle m \rangle$, of both the first and second peaks are listed in Table 2. For the first peak for all glasses and the second peak for $x = 15$ and 20 mol. %, it was found that $\langle n \rangle \neq \langle m \rangle$, which means that no nuclei exist in the as-prepared glasses. However, for $x = 5$ and 10 mol. % at the second peak, $\langle n \rangle = \langle m \rangle$, which indicates the formation of a sufficient number of nuclei during the preparation of these samples. Furthermore, the value of $\langle n \rangle$ is close to 2 for both peaks. The kinetic exponent provides information about the mechanism of crystallization [39,49]. The value of $\langle n \rangle$ for the as-quenched glass is consistent with the mechanism of volume nucleation with one-dimensional growth for both the first and second peaks [36]. It is known that the $n$ values reflect the dimensionality of the structure, with $n = 3$ corresponding to volume nucleation with two-dimensional growth, e.g. SiO$_2$, $n = 2$, volume nucleation, one-dimensional growth; or $n = 1$, surface nucleation, one-dimensional growth [50]. The increase in $n$ values with increase in WO$_3$ content can therefore be interpreted as a transformation of the two-dimensional borotellurite network [9] to a three-dimensional network, which contributes to the increase in $E_c$. According to Wells [46], pure crystalline WO$_3$, and hence its amorphous counterpart, has a three-dimensional structure consisting of [WO$_6$] structural units, as revealed by an $n$ value near 2. This means that crystallization of pure amorphous WO$_6$ involves

Figure 7. The crystallization rate $(d\chi/dt)_p$ as a function of temperature for the 5WO$_3$–75TeO$_2$–20B$_2$O$_3$ glass sample.
three-dimensional volume nucleation. The increase in the values of \( n \) can be attributed to an increase in both the coordination number [9] and the average cross-link density. Accordingly, it can be said that the transformation to three-dimensional structure provides the opportunity of crystallization in three-dimensions, so \( n \) will increase.

To identify the possible phases that crystallize during the thermal treatment applied to the samples, X-ray diffraction (XRD) patterns were obtained for the \( x \text{WO}_3-75\text{TeO}_2-(25-x)\text{B}_2\text{O}_3 \), \( 0 \leq x \leq 25 \text{ mol. \%} \) glasses annealed at temperatures beyond the peak of their crystallization temperatures with a heating rate of 10 K/min.
for 10 h. The diffractogram of the transformed material after the crystallization process suggests the presence of microcrystallites involving three phases. According to the ICDD View 2006 identification cards [51], these peaks can be identified as follows: (1) tellurium oxide, TeO₂; (2) borotellurite, BTeO₃.₅ [52,53]; (3) tungsten telluride, WTe₂; and (4) tellurium tungsten oxide, whereas an additional amorphous phase also remains, as shown in Figure 8.

![Diffractogram](image)

Figure 8. XRD patterns of crystallized xWO₃–75TeO₂–(25–x)B₂O₃ (0 ≤ x ≤ 25 mol. %) glass samples.

5. Conclusions

The crystallization kinetics of xWO₃–75TeO₂–(25–x)B₂O₃ (x = 0, 5, 10, 15, 20 and 25 mol. %) glasses were investigated under non-isothermal conditions applying the formal theory of transformations for heterogeneous nucleation to the experimental data obtained by DTA using continuous-heating techniques. Increasing the WO₃ content at the expense of B₂O₃ influences the crystallization kinetics through induced changes in the phase kinetics and in the compositions of the amorphous and crystalline phases. The increase of WO₃ content leads to the increase of the activation energy of glass transition and the activation energy for crystallization as an apparent result of the increase of the glass transition temperature, T_g, and the crystallization peak temperature, T_p, with increasing WO₃ content. The amount of WO₆ plays a significant role in the crystallization behavior of the borotellurite glasses through the interrelating TeO₂ and B₂O₃ phases. The phases into which the glass crystallizes...
have been identified by X-ray diffraction. Diffractograms of the transformed material indicate the presence of microcrystallites of TeO$_2$, BTeO$_{3.5}$, WTe$_2$ and Te$_{0.95}$W$_{0.05}$O$_{2.5}$, whereas an additional amorphous phase also remains.

References

[51] ICDD View, 2006 release. Card Nos. 00-018-0755, 01-074-0054, 01-077-0295, 00-022-0421, 00-024-0668.