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Thermal and microstructural characterization and crystallization kinetic studies in the $TeO_2-B_2O_3$ system

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HIGHLIGHTS

- The glass forming range of the system was determined as 5–25 mol% B_2O_3.
- The monotectic reaction: $liquid_1 \rightarrow liquid_2 + TeO_2$, was detected at 666 ± 2 °C.
- α-TeO_2 and B_2O_3 phases were observed as spherical and multilayered crystallites.
- Transparent phases were rich in TeO_2, while the opaque phases were rich in B_2O_3.
- The E_A value of the crystallization reaction was calculated as around 300 kJ mol^{-1}.

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ABSTRACT

Thermal, phase and microstructural characterization of the $(1-x)TeO_2-xB_2O_3$ system, where $0.05 \leq x \leq 0.40$ in molar ratio, was realized by applying differential thermal analysis, differential scanning calorimetry, X-ray diffraction and scanning electron microscopy/energy dispersive X-ray spectrometer techniques to investigate the glass forming region, phase equilibria, microstructural characterization of the $TeO_2-B_2O_3$ system and to study the crystallization kinetics of the boro-tellurite glasses. Samples were prepared using a conventional melt quenching technique at 750 °C. Glass forming range of the system was determined as 5–25 mol% B_2O_3 and thermal behavior of the glasses were examined by running thermal analysis. In order to obtain the thermal equilibrium, as-cast samples were heat-treated above all crystallization reaction temperatures at 520 °C and the phase equilibria investigations were realized with the heat-treated samples. Monotectic reaction of the binary system: $liquid_1 \rightarrow liquid_2 + TeO_2$, was detected at 666 ± 2 °C. A stable phase separation region where the samples show two different phases, white colored opaque and light yellow transparent, was investigated in terms of the phase equilibria and the morphology. Non-isothermal investigation of crystallization kinetics of the boro-tellurite glasses were realized in terms of the crystallization mechanism and the activation energy by using the Ozawa and the modified Kissinger techniques, respectively. The activation energy of the crystallization reaction was calculated as around 300 kJ mol^{-1}.

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1. Introduction

Tellurite glasses have become remarkably important for their potential use in optical applications owing to their advantageous optical properties, such as high refractive index, relatively low phonon energy and wideband infrared transmittance. Such properties make tellurite glasses suitable materials for different usage areas including optical data storage, lasers, sensors and spectroscopic applications [1–11].

Tellurium oxide (TeO_2) is a conditional glass former which forms glass with the addition of a secondary component, such as alkalis, heavy metal oxides and halogens [1–11]. Addition of B_2O_3, which is a good glass former, has some improving effects on thermal and chemical stability of tellurite glasses and glass forming ability of the system. Boro-tellurite glasses have potential applications especially in micro-electronics and opto-acoustics owing to their favorable optical and electrical properties [1,12,13].

$TeO_2-B_2O_3$ system has drawn attention of many researchers due to the presence of a wide phase separation region, which is scientifically interesting for the investigation of stable immiscibility gap in two glass former containing systems. Therefore, several studies were realized for the investigation of glass formation and phase equilibria of the $TeO_2-B_2O_3$ system and optical and

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structural properties of boro-tellurite glasses. Dimitriev et al. [14] determined the phase diagram of the system as eutectic-like type, including a monotectic reaction with a wide stable and metastable phase separation region. Later, Bürger et al. [12] studied the glass forming region, phase equilibria and structural investigation of the system and revised the phase diagram. Apart from these studies, Kashchieva et al. [15] carried out transmission electron microscope investigations in the system, Halimah et al. [16] studied physical properties, Sabry et al. [13] studied optical and electrical properties of boro-tellurite glasses and Barney et al. [17] realized structural investigation of the TeO_2–B_2O_3 system.

Although several studies were reported in the literature on the TeO_2–B_2O_3 system, further studies should be realized for the utilization of boro-tellurite glasses in advanced applications. Therefore, the present study aims to investigate the glass forming region, phase equilibria and microstructural characterization of the TeO_2–B_2O_3 system and the crystallization kinetics of the boro-tellurite glasses by applying systematical thermal, phase and microstructural studies. Phase separation region was investigated as transparent and opaque phases in order to identify different characteristics of the existing phases in this region.

2. Experimental

In the experimental studies, samples were prepared using a conventional melt-quenching technique in the $(1-x)TeO_2$–xB_2O_3 system, where $0.05 \leq x \leq 0.40$ in molar ratio. High purity powders of TeO_2 (99.99% purity, Alfa Aesar) and H_3BO_3 (99.5% purity, Sigma–Aldrich Company) were thoroughly mixed and powder batches of 3 g size were melted in a platinum crucible with a closed lid at 750 °C for 30 min in an electrical furnace and quenched in water bath. Chemical analysis was performed by using a Perkin Elmer Analyst 800 atomic absorption spectrometer with an error estimate of ±2% in order to check the final compositions of the samples.

Thermal behavior of the samples was investigated using differential thermal analysis (DTA) technique in a PerkinElmer™ Diamond TG/DTA, with a constant sample weight of 25 mg, in platinum pans, from room temperature to 750 °C with a heating rate of 10 °C min^{-1} under a flowing (100 ml min^{-1}) argon gas. The glass transition onset (T_g), crystallization onset and peak (T_c/T_p), monotectic onset and peak (T_{mo}/T_{mp}) and liquidus onset and peak (T_{lo}/T_{lp}) temperatures were determined from the DTA thermograms. The glass transition onset temperature was determined from the endotherms of the first heating scan since second heating scans gave similar results. The glass stability (ΔT) value, which is the temperature difference between the glass transition (T_g) and the first crystallization onset (T_c) temperatures was calculated.

According to the thermal analysis results, as-cast samples were heat-treated above the crystallization peak temperatures at 520 °C for 24 h to obtain the thermal equilibrium. Determination of the amorphous nature of the glass samples and the phase characterization of the heat-treated samples were realized by running X-ray diffraction (XRD) analysis. X-ray diffraction investigations were carried out in a Bruker™ D8 Advanced Series powder diffractometer by using Cu K_α radiation in the 2θ range from 10° to 90°. The International Centre for Diffraction Data (ICDD) files were used to identify the crystalline phases by comparing the peak positions and intensities with the reference patterns.

Scanning electron microscopy (SEM) investigations were conducted on platinum coated heat-treated bulk samples at 10 kV for the investigation of the morphology of the phases in equilibrium after the heat treatment. Microstructural investigations were carried out in JEOL™ Model JSM 5410 microscope linked with Noran 2100 Freedom energy dispersive X-ray spectrometer.

Differential scanning calorimetry (DSC) analyses were performed at different heating rates (5, 10, 15, 20 and 25 °C min^{-1}) from room temperature to 550 °C in order to study the crystallization kinetics of the boro-tellurite glasses. DSC scans of the samples were obtained from a Netzsch DSC 204 F1 (limit of detection: <0.1 μW, with an error estimate of ±1 °C) using a constant sample weight of 25 ± 1 mg in aluminum pans, under flowing (25 ml min^{-1}) argon gas.

3. Results and discussion

3.1. Thermal, phase and microstructural characterization

In this section, $(1-x)TeO_2$–xB_2O_3 system was investigated in two parts; hyper-monotectic region where $0.05 \leq x \leq 0.25$ in molar ratio and hypo-monotectic (phase separation) region where $0.30 \leq x \leq 0.40$ in molar ratio.

3.1.1. Hyper-monotectic region

As-cast samples prepared in the hyper-monotectic region of the TeO_2–B_2O_3 system were obtained as visually transparent and the color of the samples showed a change from dark to light yellow with the increase in B_2O_3 content.

Chemical analysis results of the samples given in Table 1 showed similar values with the calculated compositions.

X-ray diffraction analyses were realized with the as-cast samples in order to identify their amorphous nature and the results are shown in Fig. 1. According to the XRD patterns of the as-cast samples prepared in the hyper-monotectic region, no crystalline peaks were detected proving their amorphous structure.

The glass forming range of the system was determined as 5–25 mol% B_2O_3 composition under our experimental conditions. In the literature, different glass forming regions were reported for the TeO_2–B_2O_3 binary system. Bürger et al. [12] investigated the glass formation range of the system in detail with three subregions; clear glass with a cooling rate at about 10 K s^{-1} in 11.8–26.4 mol% of B_2O_3, glass with a cooling rate at about 1 K s^{-1} in 20–25 mol% of B_2O_3, glass and liquid phases with a microheterogeneous structure including more than 26.4 mol% B_2O_3. In another study, Kashchieva et al. [18] determined the glass formation range as 5–25.5 mol% of B_2O_3, while Sabry et al. [13] expanded it to 5–30 mol% of B_2O_3 under their experimental conditions. As it was reported in the literature, different sample preparation conditions have an effect on the glass forming ability of the tellurite glasses [19].

Thermal behavior of the glasses was investigated by applying differential thermal analysis. DTA thermograms of the as-cast samples in the hyper-monotectic region are shown in Fig. 2 and the thermal analysis data are given in Table 1. According to the DTA results, all as-cast samples showed a broad endothermic change

Table 1
Values of glass transition onset (T_g), crystallization onset and peak (T_c/T_p), monotectic onset and peak (T_{mo}/T_{mp}), liquidus onset and peak (T_{lo}/T_{lp}), glass stability (ΔT) of the as-cast samples in the hyper-monotectic region in the $(1-x)TeO_2$–xB_2O_3 system, with an error estimate of ±2 °C.

Samples	Original compositions (mol%)		Final composition (mol%)	T_g (°C)	T_c/T_p (°C)	T_{mo}/T_{mp} (°C)	T_{lo}/T_{lp} (°C)	ΔT
	TeO_2	B_2O_3	B_2O_3					
$x = 0.05$	95	5	4.44	310	353/370	667/670	698/715	43
$x = 0.10$	90	10	9.82	313	368/405	667/671	688/703	55
$x = 0.15$	85	15	14.35	331	397/411	665/670	-/691	66
$x = 0.20$	80	20	20.16	334	412/429	667/672	–	78
$x = 0.225$	77.5	22.5	22.82	335	418/438	667/671	–	83
$x = 0.25$	75	25	25.4	347	427/444	667/672	–	80

-: Undetermined values.

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