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Thermal properties and crystallization behavior of some TeO_2–K_2O glasses

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Abstract

The effect of K_2O content on the crystallization of binary TeO_2–K_2O glasses was investigated. Glasses with compositions of $(1-x)TeO_2$–xK_2O (where $x = 0.05$, 0.10, 0.15, in molar ratio) were prepared. DTA curves in the temperature range of 25–700 °C with the heating rate of 10 °C/min were used to determine the thermal properties such as glass transition temperature (T_g), crystallization peaks (T_p), and melting temperature (T_m). Crystallization peaks ranging between 364 and 421 °C were detected on the DTA scans. DTA results revealed that the most stable glasses were formed with the modifier concentrations near the eutectic composition, 0.10 mol. Crystallizing phases and microstructural morphology for each composition were characterized by XRD and SEM. On the basis of XRD measurements, α-TeO_2 (paratellurite), γ-TeO_2 and $K_2Te_4O_9$ (potassium tetratellurite) phases were detected. The $K_2Te_4O_9$ phase is present in all three glasses, due to the fact that this phase arises because of a phase separation melting of the glass.

Keywords: Microstructure; Thermal properties; Glass

1. Introduction

Tellurium oxide (TeO_2) under normal conditions does not have the ability to form glass easily without a modifier like alkali, earth alkali and other glass formers.[1] Potassium oxide (K_2O) is a strong modifier for the glass systems and it provides transparency and homogeneity.

An understanding of the thermal stability and crystallization behavior is vital to develop and use TeO_2-based glasses.[2]

Understanding of the crystallization behavior is important for TeO_2-based glasses intended for laser applications during which the glasses will bear thermal loads and thus will be subjected to crystallization.[3]

The aim of this study is to determine the thermal properties and the crystallization behavior of some $(1-x)TeO_2$–xK_2O glasses. For this purpose, three different glass compositions, viz. 0.95 TeO_2–0.05 K_2O, 0.9 TeO_2–0.1 K_2O, 0.85 TeO_2–0.15 K_2O, were investigated using DTA, X-ray diffractometry and SEM techniques.

2. Experimental procedure

2.1. Glass synthesis

Glass samples were prepared with the compositions of $(1-x)TeO_2$–xK_2O where $x = 0.05$, 0.10 and 0.15 in molar ratio (now hereafter referred to as the 0.95 TeO_2–0.05 K_2O, 0.9 TeO_2–0.1 K_2O, 0.85 TeO_2–0.15 K_2O glasses, respectively). Powders of reagent-grade K_2CO_3 (99.995% purity, Chempur Co.) and TeO_2 (99.995% purity, Chempur Co.) were used as starting materials. Batches of 7 g in size were thoroughly mixed and melted using a platinum crucible with a closed lid in an electrically heated furnace at 900–950 °C for 30 min, until CO_2 evolution ceased. To achieve homogeneity, the cast was crushed, pulverized and reheated at the same temperature for additional 30 min. Following that, the melts were removed from the furnace at 950 °C and quenched by immersing the crucible in a shallow water bath.

2.2. Thermal behavior and microstructural characterization

Differential thermal analysis (DTA) scans of as-cast glass specimens were carried out in Thermoflex Rigaku thermal

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analyzer equipped with PTC-10A temperature controller unit to determine the characteristics glass transition temperatures (T_g), crystallization peaks (T_p), and melting temperature (T_m). The glass powder, 50 mg, were heated at the rate of 10 °C/min from room temperature to 700 °C in a platinum crucible and using the same amount of alumina powder as the reference material. Identification of the crystallized phases were determined by X-ray diffraction (XRD) techniques by using a Philips^{TM} model PW3710 (Cu Kα radiation) diffractometer setting in the 2θ range from 10° to 90°. The crystallized phases were identified by comparing the peak positions and intensities with those in the JCPDS (joint committee on powder diffraction standards) data files. Scanning electron microscopy (SEM) investigations were conducted in JEOL^{TM} JSM 5410 operated at 15 kV and linked with Noran 2100 freedom energy dispersive spectrometer (EDS) attachment. Optical mount specimens were prepared using standard metallographic techniques followed by etching in a 5% HF solution for 20–30 s and coated with carbon.

3. Results and discussion

The range of glass formation in the binary tellurite glasses have been documented in the "Tellurite Glasses Handbook"[4] for K_2O content between 0.025 and 0.345 mol although some variation is possible depending upon the exact method of sample preparation. After a series of preliminary X-ray diffractometry tests, three compositions of $(1-x)TeO_2$–xK_2O glass system with $x = 0.05$, 0.10 and 0.15 mol were chosen which yielded successful glass formation, depending on the classical quenching method. The glass formation is favored at eutectic compositions[5] and TeO_2–K_2O glass system exhibits an eutectic phase at exactly 0.90 TeO_2–0.10 K_2O glass composition.

Differential thermal (DTA) investigations were conducted on the as-cast TeO_2–K_2O glasses. Each DTA scan exhibit a small endothermic peak corresponding to the glass transition temperature, T_g, at 310 °C for the 0.95 TeO_2–0.05 K_2O glass, at 295 °C for the 0.9 TeO_2–0.1 K_2O glass and at 275 °C for the 0.85 TeO_2–0.15 K_2O glass (Fig. 1(a)–(c), respectively). The increase in the K_2O content leads to the decrease of the glass transition temperature values. This result suggests that K_2O acts as a network modifier and TeO_2 acts as the network former. Crystallization processes are marked by single exothermic peaks at 394 °C for the 0.95 TeO_2–0.05 K_2O and at 421 °C for the 0.9 TeO_2–0.1 K_2O glass. Two exothermic peaks occurring at 364 and 418 °C were observed for the 0.85 TeO_2–0.15 K_2O glass (Fig. 1(c)) and it is evident that both peaks can be attributed to the formation and/or transformation of crystalline phases.

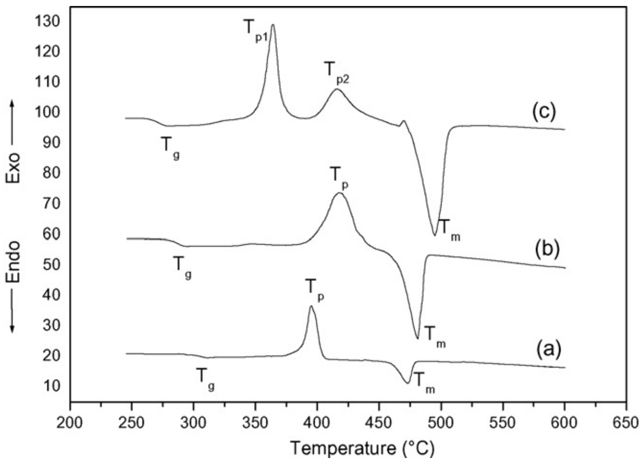

Fig. 1. DTA curves of as-cast samples of 0.95 TeO_2–0.05 K_2O glass (a), 0.9 TeO_2–0.1 K_2O glass (b) and 0.85 TeO_2–0.15 K_2O glass (c) scanned at a rate of 10 °C/min.

Glass forming tendency, K_g, given by Eq. (1), can be determine in order to compare devitrification tendency of the glasses. Low values of K_g suggests high tendency of crystallization:[6]

$$K_g = \frac{T_c - T_g}{T_m - T_c} \tag{1}$$

Glass forming tendency values are calculated by using the temperatures, T_g, T_p, T_m (Table 1), obtained from DTA curves of the 0.95 TeO_2–0.05 K_2O, 0.9 TeO_2–0.1 K_2O and 0.85 TeO_2–0.15 K_2O glasses scanned at a rate of 10 °C/min. As seen in Table 1, 0.9 TeO_2–0.1 K_2O is the most susceptible to form glass among three compositions, with a K_g value of 2.06.

On the basis of DTA results (Fig. 1), XRD scans were carried out to identify the crystallizing phases in the glassy matrix above the peak temperatures for all compositions. Fig. 2(a)–(c) are the XRD patterns taken from the heat-treated and the as-cast samples of the 0.95 TeO_2–0.05 K_2O, 0.9 TeO_2–0.1 K_2O and 0.85 TeO_2–0.15 K_2O glasses, respectively. The heat-treated glass samples were prepared by heating the as-cast glasses 10–15 °C above the crystallization peak temperature for 30 min, followed by quenching in air.

Hart[7] reported that the formation of the $K_2Te_4O_9$ phase, as a result of a phase separation in TeO_2–K_2O glasses with varying between 5 and 30 mol% K_2O content. This phase which has the same symmetry as the crystal, $P2_1/c$, which is a centrosymmetric monoclinic space group but the lattice is tetragonal, with lattice parameters of 0.757, 0.773 and 1.782 nm, This is the reason why the $K_2Te_4O_9$ phase is detected in the XRD scans (Fig. 2) of heat-treated and as-cast samples of TeO_2–K_2O glasses in the present investigation. In other words, the diffraction angle values (2θ) of 12.5°, 15° and 20° detected in all figures of Fig. 2 are the characteristic angles for the $K_2Te_4O_9$ phase.[8] The XRD pattern of the 0.95 TeO_2–0.05 K_2O glass crystallized at 425 °C (Fig. 2(a)) reveals the presence of the γ-TeO_2 and α-TeO_2 phases in addition to the $K_2Te_4O_9$ phase. Whereas the stable α-TeO_2 phase (paratellurite) has a tetragonal crystal structure with lattice parameters $a = 0.481$ nm and $c = 0.761$ nm,[9]

Table 1
Values of glass forming tendency, K_g, and glass transition, T_g, crystallization, T_p and melting, T_m, temperatures of the $(1-x)TeO_2$–xK_2O glasses

K_2O content (mol%)	T_g (°C)	T_{p1} (°C)	T_{p2} (°C)	T_m (°C)	$K_g = \frac{(T_c-T_g)}{(T_m-T_c)}$
5	310	394	–	472	1.07
10	297	421	–	481	2.06
15	275	364	418	485	0.73

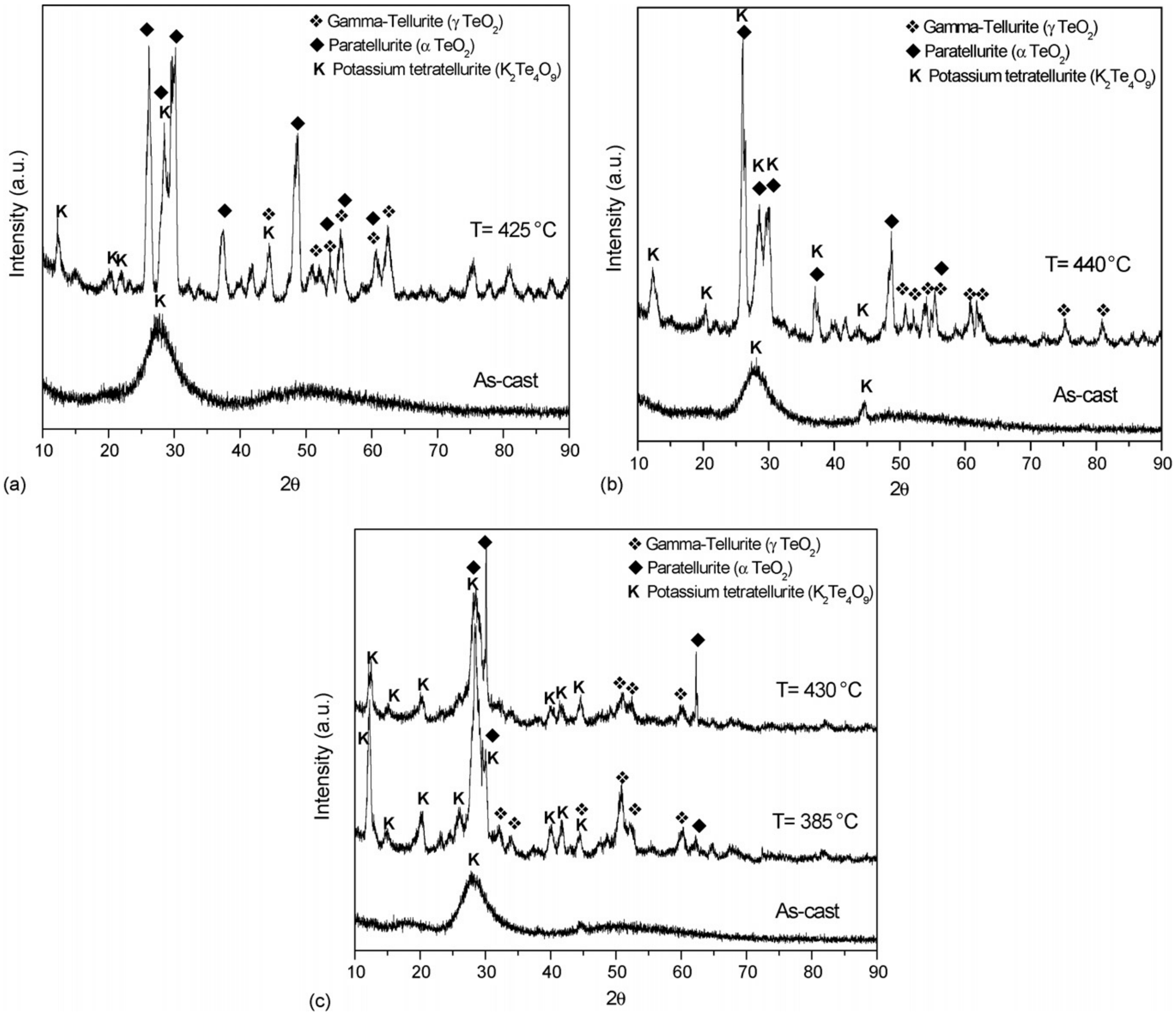

Fig. 2. XRD scans taken from: (a) the 0.95 TeO_2–0.05 K_2O glass in the as-cast condition and after heat-treating at 425 °C; (b) the 0.9 TeO_2–0.1 K_2O glass in the as-cast condition and after heat-treating at 440 °C; (c) the 0.85 TeO_2–0.15 K_2O glass in the as-cast condition and after heat-treating at 385 and 430 °C.

metastable phase has an orthorhombic crystal structure with lattice parameters $a = 0.845$ nm, $b = 0.499$ nm and $c = 0.430$ nm.[10] On the basis of XRD pattern of 0.9 TeO_2–0.1 K_2O sample heat-treated at 440 °C (Fig. 2(b)) comprise the α-TeO_2, γ-TeO_2 and $K_2Te_4O_9$ phases similar to the 0.95 TeO_2–0.05 K_2O sample. Fig. 2(c) shows the XRD pattern of the 0.85 TeO_2–0.15 K_2O glass in the as-cast condition and crystallized at 385 and 430 °C. All three crystallizing phases (α-TeO_2, γ-TeO_2 and $K_2Te_4O_9$) co-exist at 385 °C (above the first exotherm in Fig. 1), as expected. On the other hand, the amount of γ-TeO_2 decreased the 430 °C inferring that the second exotherm in Fig. 1 is a result of γ-TeO_2 → α-TeO_2 transformation. Existence of $K_2Te_4O_9$ and TeO_2 phases were also verified by SEM and EDS analyses.

SEM investigations were also performed for the heat-treated samples to identify the morphology of the resultant microstructures after crystallization. All SEM micrographs are taken in the secondary electron imaging (SEI) mode.

Fig. 3(a) is a representative SEM micrograph of the 0.95 TeO_2–0.05 K_2O glass samples heated to 425 °C followed by air-quenching. EDS analyses taken from the elongated crystalline regions (85.2 ± 0.5 wt.% Te, 0.08 ± 0.4 wt.% K and 13 ± 0.4 wt.% O) confirms that the crystalline regions are composed of a TeO_2 phase.

Fig. 3(b) is a SEM micrograph of the 0.9 TeO_2–0.1 K_2O sample heat-treated at 440 °C showing square-shaped crystals varying between 7 and 10 μm width, 7 and 10 μm in length. EDS analyses taken from three different locations (regions B in Fig. 3(b)) show that these crystals contained 74.2 ± 0.3 wt.% Te, 6.5 ± 0.4 wt.% K and 18.2 ± 0.3 wt.% O, indicating that the crystals consist of the TeO_2 and $K_2Te_4O_9$ phases.

Fig. 3(c) is a SEM micrograph of 0.85 TeO_2–0.15 K_2O glass, heat-treated at 385 °C (first exotherm in Fig. 1). EDS spectra taken from the crystalline structures (regions C in Fig. 3(c)) shows that the amorphous glass matrix in the bulk of the

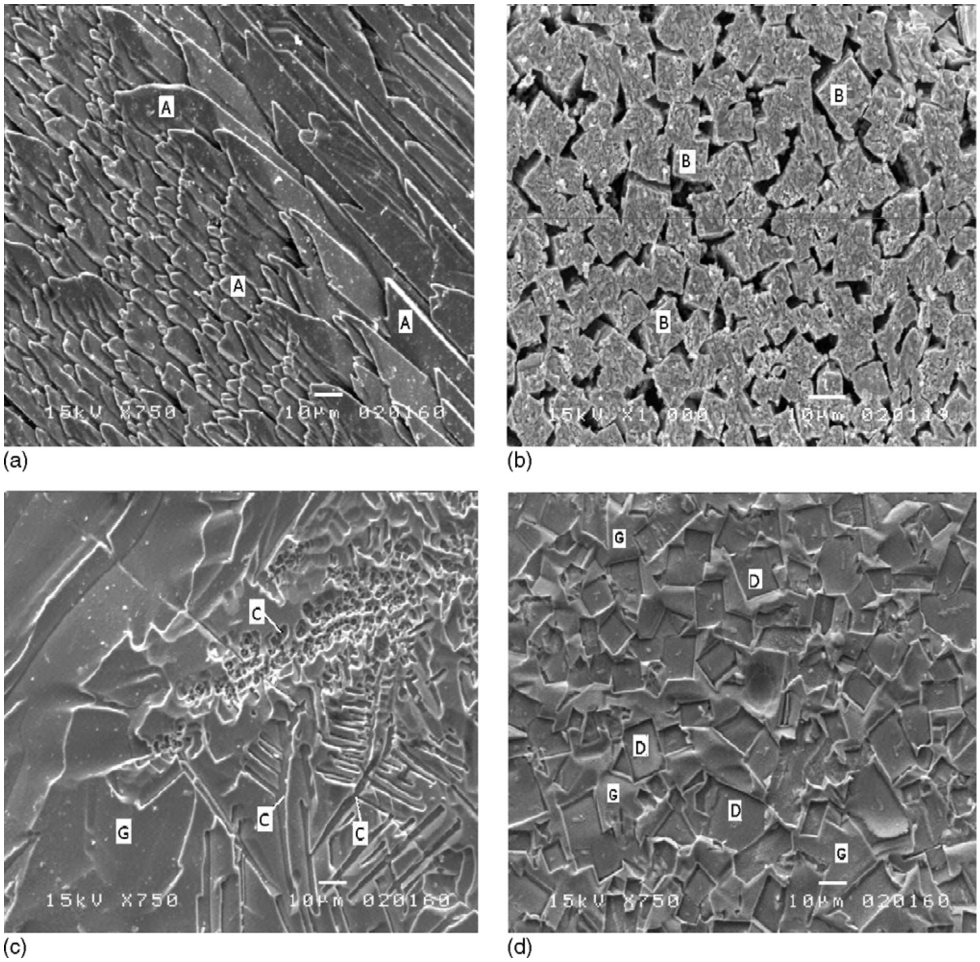

Fig. 3. Typical SEM micrographs taken from the crystalline regions of (a) the 0.95 TeO_2–0.05 K_2O sample heat-treated at 425 °C; (b) 0.9 TeO_2–0.1 K_2O sample heat-treated at 440 °C; (c) the 0.85 TeO_2–0.15 K_2O sample heat-treated at 385 °C and (d) the same glass heat-treated at 430 °C.

sample contained 85.2 ± 0.3 wt.% Te, 5.5 ± 0.3 wt.% K, 9.8 ± 0.5 wt.% O.

Fig. 3(d) is a SEM micrograph from different locations of the 0.85 TeO_2–0.15 K_2O sample crystallized at 430 °C, showing rectangular-shaped crystals stacked in 2D-orientation having crystal sizes ranging between 5 and 10 µm in width, 5 and 15 µm in length. EDS spectra taken from the crystalline regions (regions D in Fig. 3(d)) shows that the regions had the chemical stoichiometry of 67.7 ± 0.5 wt.% Te, 11.2 ± 0.5 wt.% K and 21.3 ± 0.4 wt.% O, indicating that these are $K_2Te_4O_9$-rich crystals surrounded by a glassy matrix, regions G.

4. Conclusions

In this study, thermal properties of $(1 - x)TeO_2$–xK_2O binary glasses were investigated in order to examine the effect of K_2O content. According to glass forming tendency values the glass having a K_2O concentration of roughly 0.10 mol is the easiest to form glass. The peak crystallization temperatures vary from 364 to 421 °C with the increase in the heating rate. Two exotherms were observed in the DTA curves of 0.85 TeO_2–0.15 K_2O glass while the 0.95 TeO_2–0.05 K_2O and 0.9 TeO_2–0.1 K_2O glasses having one for each.

XRD investigations shows that, all the heat-treated glasses contains $K_2Te_4O_9$, α-TeO_2 and γ-TeO_2 phases at varying amounts according to the composition and increase in the amount of K_2O content inhibits the crystallization of the TeO_2 phase. SEM studies reveals; the second exotherm is associated to the crystallization of the $K_2Te_4O_9$ phase for the 0.85 TeO_2–0.15 K_2O glass, while the TeO_2 phase is dominant for the 0.95 TeO_2–0.05 K_2O glass.

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