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Phase equilibria and glass formation studies in the $(1-x)TeO_2$–$xCdO$ $(0.05 \leq x \leq 0.33\,mol)$ system

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Abstract

Phase equilibria and glass formation studies of the $(1-x)TeO_2$–$xCdO$ system $(0.05 \leq x \leq 0.33\,mol)$ were realized by using differential thermal analysis (DTA), X-ray diffraction (XRD) and scanning electron microscopy (SEM) techniques. The samples were prepared by applying a conventional melt-quenching technique at 800 °C. The glass formation range of the system was determined as $0.05 \leq x < 0.15$ and the sample containing 10 mol% CdO showed the highest glass stability. Crystallization behavior of the TeO_2–CdO glasses was investigated and formation and/or transformation of different phases were detected for each crystallization reaction. In order to obtain thermal stability of the system, as-cast samples were heat-treated above all crystallization reaction temperatures at 550 °C for 24 h. A binary eutectic: liquid → $TeO_2 + CdTe_2O_5$ was detected at 638 ± 4 °C. Crystallization behavior of the TeO_2–CdO glasses and microstructural characterization of the TeO_2–$CdTe_2O_5$ system was realized.

Keywords: TeO_2–$CdTe_2O_5$; Glass; Thermal properties; Microstructure-final

1. Introduction

Tellurite glasses have a great potential to be used in optics, photonics and opto-electronic applications due to their favorable properties; such as low melting point, good thermal and chemical stability, low crystallization ability, low phonon energy, high refractive index and dielectric constant and good infrared transmission.[1–8]

TeO_2, as a pure oxide, does not form glass under normal cooling conditions; therefore addition of a secondary component (alkalis, halogens, heavy metal oxides, etc.) is necessary to increase the glass forming tendency via modifying the network structure by introducing non-bridging oxygen sites.[1,3,5–8] In the present study CdO was selected as the network modifier since it enhances the optical properties by stabilizing the glass structure and improves the electrical properties by increasing the dielectric constant.[9,10]

In the literature, the partial phase diagram of the TeO_2–CdO system was constructed by Robertson et al.[11] The glass formation range of the system was reported by Mochida et al.[12] as 5–10 mol% CdO. Moreover, Komatsu and Mohri[13] and Zayas et al.[9] reported that the TeO_2–CdO system has a very narrow glass forming region and the glasses prepared in this system are partially crystallized. However, there exist no information on the thermal measurement data and microstructural characterization of the system and the crystallization behavior of the TeO_2–CdO glasses was not investigated in the literature.

As part of an ongoing research on tellurite based glasses in the TeO_2–WO_3–CdO system, the present study aims to investigate the phase equilibria and the glass formation range of the TeO_2–CdO system within the TeO_2–$CdTe_2O_5$ region by applying systematical thermal, phase and microstructural characterizations. Apart from obtaining the glass formation range and the phase equilibria of the binary system which are almost in agreement with the literature, for the first time to our best knowledge the crystallization behavior of the TeO_2–CdO glasses was investigated and the microstructural characterization of the system was realized.

2. Experimental

In the experimental studies, samples were prepared with the compositions of $(1-x)TeO_2$–$xCdO$, where x varies between

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0.05 and 0.33 in molar ratio (now hereafter referred to as *TC*5–*TC*33 samples, according to their CdO mol%). High purity powders of TeO_2 (%99.99 purity, Alfa Aesar) and CdO (%99.95 purity, Alfa Aesar) were thoroughly mixed and 5 g size powder batches were melted in a platinum crucible with a closed lid at 800 °C for 30 min in an electrical furnace and quenched in water bath. Thermal characterization experiments were realized using differential thermal analysis (DTA) technique. DTA analyses were carried out in a PerkinElmer^{TM} Diamond TG/DTA instrument by using 25 mg of powdered samples with a heating rate of 10 °C/min in platinum pans in a flowing (100 ml/min) argon gas atmosphere. The glass transition (T_g), crystallization onset and peak (T_c/T_p), eutectic onset and peak (T_e/T_m), liquidus onset and peak (T_{lo}/T_{lp}) temperatures were determined from the DTA scans. The temperature difference between the T_g and the first exothermic peak onset (T_{c1}), $\Delta T = T_{c1} - T_g$, indicating the glass stability against crystallization was calculated for glass samples. The glass transition onset temperature was taken as the inflection point of the endothermic change of the calorimetric signal. Onset temperatures were determined where exothermic or endothermic reactions begin and peak temperatures were specified at the maximum value of the exotherm or endotherm. X-ray diffraction analyses were realized in a Bruker^{TM} D8 Advanced Series powder diffractometer using Cu Kα radiation. The International Centre for Diffraction Data (ICDD) files were used to determine the crystalline phases by comparing the peak positions and intensities with the reference patterns. Microstructural characterization of the samples was conducted with gold/platinum coated bulk samples in JEOL^{TM} Model JSM 5410 and JEOL^{TM} Model JSM 7000F scanning electron microscopes.

To recognize the thermal and structural behavior of the samples, DTA and XRD analyses were carried out with all as-cast samples. After determining the glass formation range of the system, the crystallization behavior of the TeO_2–CdO glasses was investigated by heat-treating the *TC*10 glass sample above each exothermic reaction onset temperature for 24 h (at 335, 370, 425 and 550 °C) to obtain the thermal equilibrium of the existing phases. Afterwards, XRD and SEM analyses were carried out on as-cast and heat-treated *TC*10 sample to investigate the crystallization behavior of the TeO_2–CdO glasses. For the phase equilibria studies, all as-cast samples were heat-treated for 24 h at 550 °C above the crystallization peak temperatures to obtain the thermal stability of the system. DTA, XRD and SEM analyses were performed in order to identify the equilibrium phases.

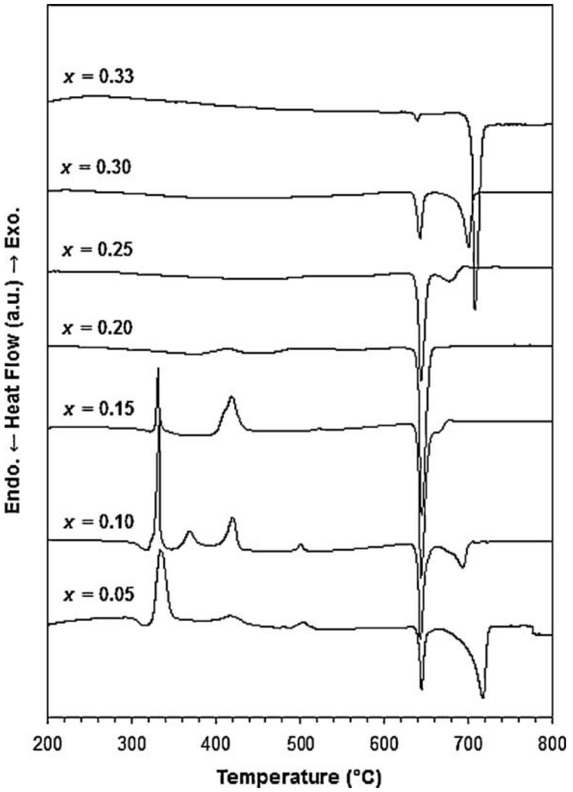

Fig. 1. DTA curves of as-cast samples of $(1-x)TeO_2$–xCdO, where x varies between 0.05 and 0.33, in molar ratio.

3. Results and discussion

3.1. Characterization of the as-cast samples

DTA analyses of as-cast $(1-x)TeO_2$–xCdO samples, where x varies from 0.05 to 0.33 are presented in Fig. 1 and the thermal analysis details are given in Table 1.

Table 1

Values of glass transition onset (T_g), crystallization onset and peak (T_c/T_p), eutectic onset and peak (T_e/T_m), liquidus onset and peak (T_{lo}/T_{lp}), with an error estimate of ±3 °C.

Sample ID	Compositions (mol%)		T_g	T_{c1}/T_{p1}	T_{c2}/T_{p2}	T_{c3}/T_{p3}	T_{c4}/T_{p4}	T_e/T_m	T_{lo}/T_{lp}
	TeO_2	CdO							
*TC*5	0.95	0.05	303	325/335	398/418	492/504		642/645	–/718
*TC*10	0.90	0.10	304	327/330	358/368	410/420	495/501	639/644	–/694
*TC*15	0.85	0.15	309	328/331	404/419	510/522		640/644	–/666
*TC*20	0.80	0.20		390/415	472/496			640/645	
*TC*25	0.75	0.25						639/644	–/679
*TC*30	0.70	0.30						637/642	–/701
*TC*33	0.67	0.33						634/639	704/708

(–) Undetermined values.

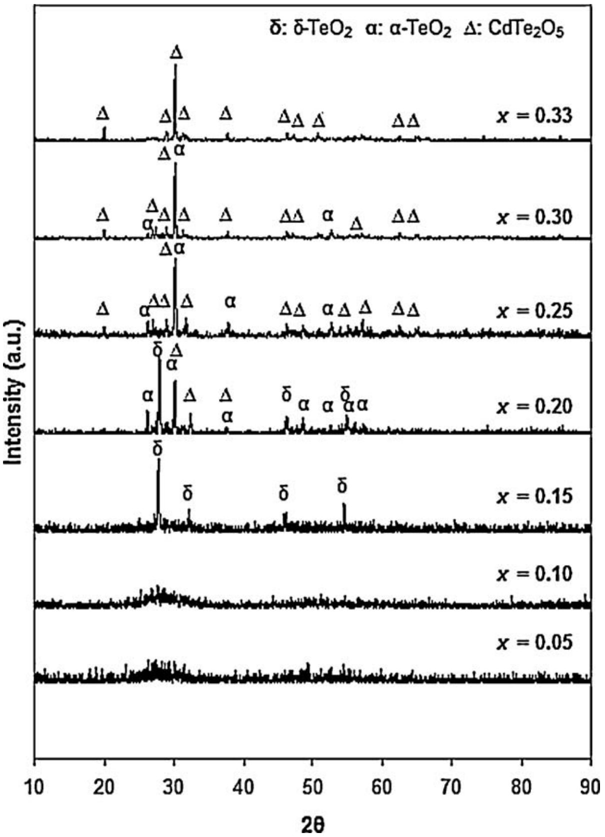

Fig. 2. XRD patterns of as-cast samples of $(1-x)TeO_2$–$xCdO$, where x varies between 0.05 and 0.33 in molar ratio.

For the *TC*5, *TC*10, *TC*15 samples, a broad endothermic change of the calorimetric signal corresponding to the glass transition reaction was observed between 303 and 309 °C. Several exothermic peaks related to the crystallization and/or transformation of different phases was detected. As can be seen from Fig. 1, the number of exothermic reactions observed in DTA thermograms varies with the composition. The glass transition and the first crystallization onset temperatures were found to be close to each other; however it was reported in the literature that the substitution of CdO for TeO_2 greatly increased the T_g and T_{c1} values.[13]

The glass stability parameter, which provides a good estimate of glass crystallization tendency, was calculated for the *TC*5, *TC*10, *TC*15 samples and the maximum ΔT value was found as 23 °C for *TC*10 sample. The ΔT values obtained in the present study for TeO_2–CdO glasses were found to be lower than the glass stability values reported in the literature for other tellurite based binary glasses.[1]

An endothermic reaction indicating the eutectic reaction of the TeO_2–$CdTe_2O_5$ binary system (liquid → α-TeO_2 + $CdTe_2O_5$) was determined for all as-cast samples. Onset and peak temperatures of the eutectic reaction were determined as 638 ± 4 °C and 642 ± 3 °C, respectively (see Fig. 1 and Table 1). In the literature, the eutectic reaction temperature was detected approximately at the similar values by Robertson et al.[11] The second endothermic peaks related to the liquidus reaction shifted towards the eutectic composition with the changing CdO content.

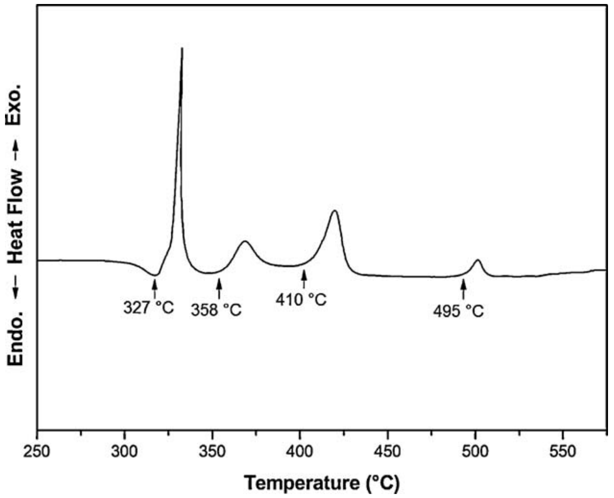

Fig. 3. DTA curve of as-cast *TC*10 sample.

X-ray diffraction analysis results of the as-cast samples are given in Fig. 2. As can be seen from Fig. 2, XRD patterns of the as-cast *TC*5 and *TC*10 samples revealed no detectable peaks, proving the amorphous glassy structure of the as-cast samples. However, for the as-cast *TC*15 sample, which was obtained transparent at macro size and showed a glass transition reaction in the DTA scan, the XRD result revealed the formation of δ-TeO_2 phase. This might be resulted due to the crystallization of δ-TeO_2 phase on the surface from the glass matrix as reported in our earlier study.[5] Consequently, the glass formation range of the system was determined as $0.05 \leq x < 0.15$, however as it was reported in the literature by Komatsu and Mohri[13] and

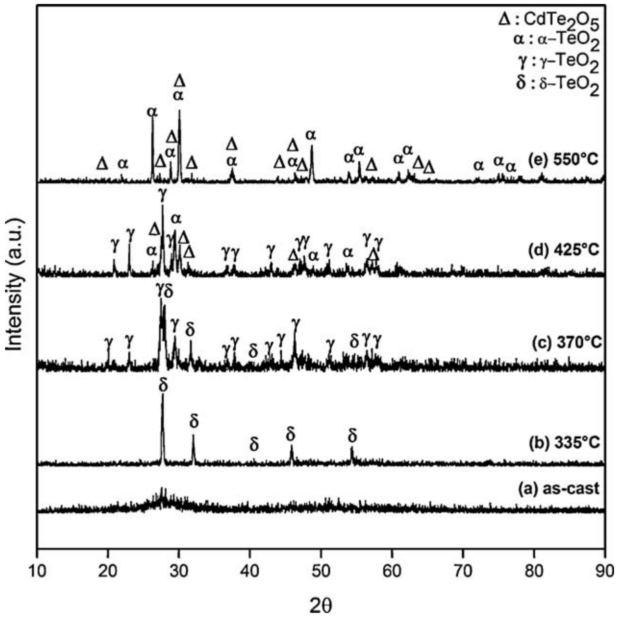

Fig. 4. XRD patterns of *TC*10 glass sample (a) as-cast, and heat-treated for 24 h at (b) 335 °C, (c) 370 °C, (d) 425 °C, (e) 550 °C.

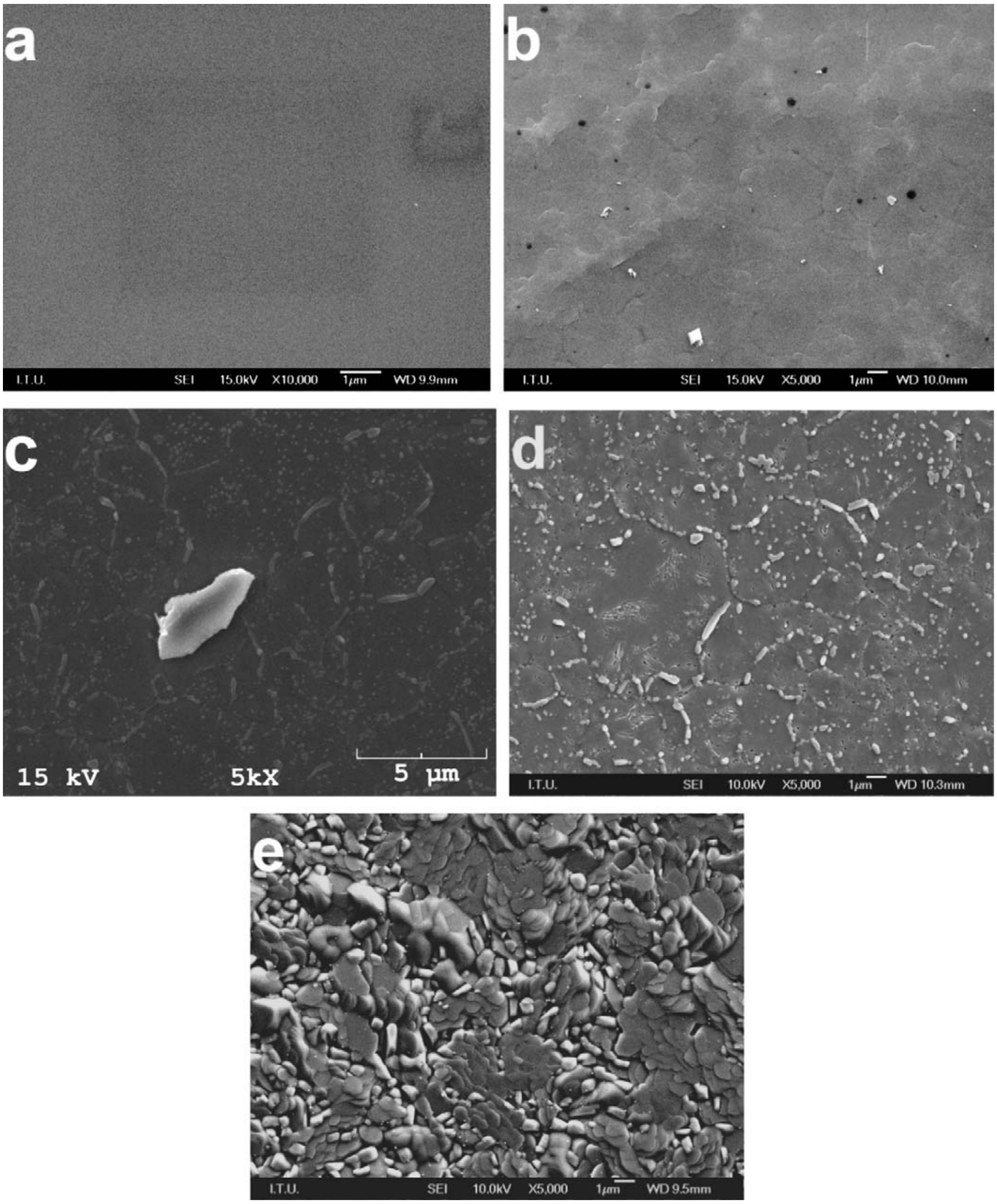

Fig. 5. SEM images of *TC*10 sample (a) as-cast, (b) heat-treated at 335 °C, (c) heat-treated at 370 °C, (d) heat-treated at 425 °C, (e) heat-treated at 550 °C.

Zayas et al.,[9] the glasses prepared in this system can be partially crystallized, therefore special cooling conditions might be required to obtain homogenous glass samples. The glass formation range of the TeO_2–CdO binary system was first reported in the literature by Mochida et al.[12] as 5–10 mol% CdO, however according to our experimental results it was understood that the glass formation range of this system can be expanded to 5–15 mol% CdO. As seen in Fig. 2, for *TC*20 sample δ-TeO_2, α-TeO_2 and $CdTe_2O_5$ phases were crystallized in the structure. For the samples with higher CdO content ($x \geq 0.25$), δ-TeO_2 phase was no longer detected and α-TeO_2 and $CdTe_2O_5$ phases were crystallized in the structure. With increasing CdO content, $CdTe_2O_5$ phase became more pronounced and for *TC*33 sample, only $CdTe_2O_5$ phase was crystallized in the structure.

3.2. Crystallization behavior of TeO_2–CdO glasses

To investigate the crystallization behavior of TeO_2–CdO glasses, *TC*10 sample was selected since it exhibits better glass forming ability compared to other glass forming compositions. DTA scan of the as-cast *TC*10 sample is given in the temperature range of 250–550 °C in Fig. 3. As seen in Fig. 3, a slight endothermic change corresponding to the glass transition reaction (T_g) was detected at 303 °C and followed by four exothermic reactions with the onset temperatures at 327, 358, 410 and 495 °C, respectively.

According to the DTA results, as-cast *TC*10 sample was heat-treated above each exothermic onset temperature for 24 h (at 335, 370, 425 and 550 °C) to achieve the thermal equilibrium of the crystalline phases. Afterwards, XRD analyses were realized to identify the crystallized phases for each exothermic reaction detected in the DTA analysis and the XRD analysis results of *TC*10 glass sample are given in Fig. 4. As can be seen from Fig. 4, XRD pattern of as-cast *TC*10 sample confirmed the amorphous nature of the glass structure. After heat-treating the sample at 335 °C, a good match was found between the observed peak positions and the card values of metastable δ-TeO_2 phase. Therefore, it was realized that the first exothermic reaction detected in the DTA scan is related to the crystallization of metastable δ-TeO_2 phase from the glass matrix. The formation of cubic δ-TeO_2 phase with the addition of CdO into tellurite glasses causes low glass stability values for TeO_2–CdO glasses, which was also reported in our previous study.[5] XRD results of *TC*10 sample heat-treated at 370 °C revealed the formation of another metastable phase, γ-TeO_2, with the existing δ-TeO_2 phase. This shows that the second exothermic reaction observed in the DTA scan belongs to the formation of metastable γ-TeO_2 phase. For the sample heat treated at 425 °C, δ-TeO_2 phase was no longer observed in the structure due to the transformation of metastable δ-TeO_2 to stable α-TeO_2 phase and $CdTe_2O_5$ phase was formed in the structure with the existing γ-TeO_2 phase. Therefore, the XRD result proved that the third exothermic reaction observed in the DTA thermogram corresponds to the transformation of δ-TeO_2 into α-TeO_2 phase and the formation of $CdTe_2O_5$ phase. When the sample was heat-treated at 550 °C to achieve the thermal equilibrium of the binary system, α-TeO_2 and $CdTe_2O_5$ phases were found to be present in the system. Therefore, XRD result confirmed that the fourth exothermic reaction observed in the DTA scan is related to the transformation of metastable γ-TeO_2 phase into stable α-TeO_2 phase and the formation of $CdTe_2O_5$ phase.

In consequence of the XRD investigations it was understood that for TeO_2–CdO glasses, δ-TeO_2 phase was crystallized from the glass matrix at around 335 °C and the formation of γ-TeO_2 phase was observed at about 370 °C. Transformation of δ-TeO_2 phase into α-TeO_2 was observed at around 425 °C and γ-TeO_2 phase was transformed into α-TeO_2 phase when the thermal equilibrium was achieved at 550 °C. Similar crystallization behavior was also observed in the literature for different tellurite-based glasses.[2,5,14,15]

SEM investigations were conducted on as-cast and heat-treated *TC*10 sample in order to identify the morphology of the crystallized phases in TeO_2–CdO glasses. Microstructural morphology of the TeO_2–CdO glasses was detected for the first time in the literature and the SEM micrographs of as-cast and heat-treated (at 335, 370, 425 and 550 °C) *TC*10 sample are given in Fig. 5a–e.

The SEM micrograph of the as-cast *TC*10 sample (see Fig. 5a) revealed no crystallization, proving the glassy nature of the sample. As can be seen from Fig. 5b, the micrograph shows grain-like crystallites on the surface for *TC*10 sample heat-treated at 335 °C. XRD analysis of this sample (see Fig. 4) showed the formation of δ-TeO_2 phase from the glassy matrix, therefore it is concluded that the grain-like crystallites observed in the SEM micrograph (Fig. 5b) is due to the formation of δ-TeO_2 phase on the surface. The SEM micrograph of the *TC*10 sample heat-treated at 370 °C (see Fig. 5c) showed that the δ-TeO_2 phase is still present as grain-like crystallites and γ-TeO_2 phase is formed as worm-like crystallites. As can be seen from Fig. 5d, the SEM image of *TC*10 sample heat-treated at 425 °C showed that the grain-like crystallites which belong to the δ-TeO_2 phase were no more detected, γ-TeO_2 phase is still present as worm-like crystallites and large grain-like crystallites were started to form on the surface possibly due to the formation of $CdTe_2O_5$ phase in the structure. SEM micrograph of *TC*10 sample heat-treated at 550 °C shown in Fig. 5e reveals that a grain-like crystallization corresponding to α-TeO_2 and $CdTe_2O_5$ phases occurred in the general structure when the final crystallization was achieved.

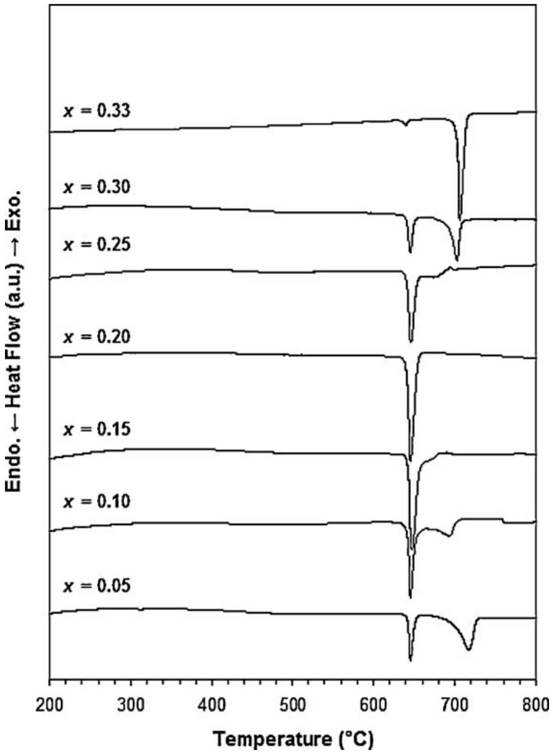

Fig. 6. DTA curves of $(1-x)TeO_2$–xCdO samples heat-treated at 550 °C for 24 h, where x varies between 0.05 and 0.33, in molar ratio.

3.3. *Characterization of the heat-treated samples*

For the phase equilibria studies, as-cast samples were heat-treated above all crystallization peak temperatures at 550 °C in order to obtain the thermal equilibrium (see Fig. 1). According to the DTA results of the heat-treated samples shown in Fig. 6, no exothermic reaction was detected proving that the crystallization and/or transformation of different phases were completed and the thermal equilibrium condition was achieved.

An endothermic reaction representing the eutectic reaction (liquid → $TeO_2 + CdTe_2O_5$) of the TeO_2–$CdTe_2O_5$ binary system was determined. Onset and peak temperatures of the eutectic reaction were determined as 638 ± 4 °C and 644 ± 3 °C, respectively. As it was observed for the as-cast samples, the second endothermic peaks related to the liquidus reaction shifted

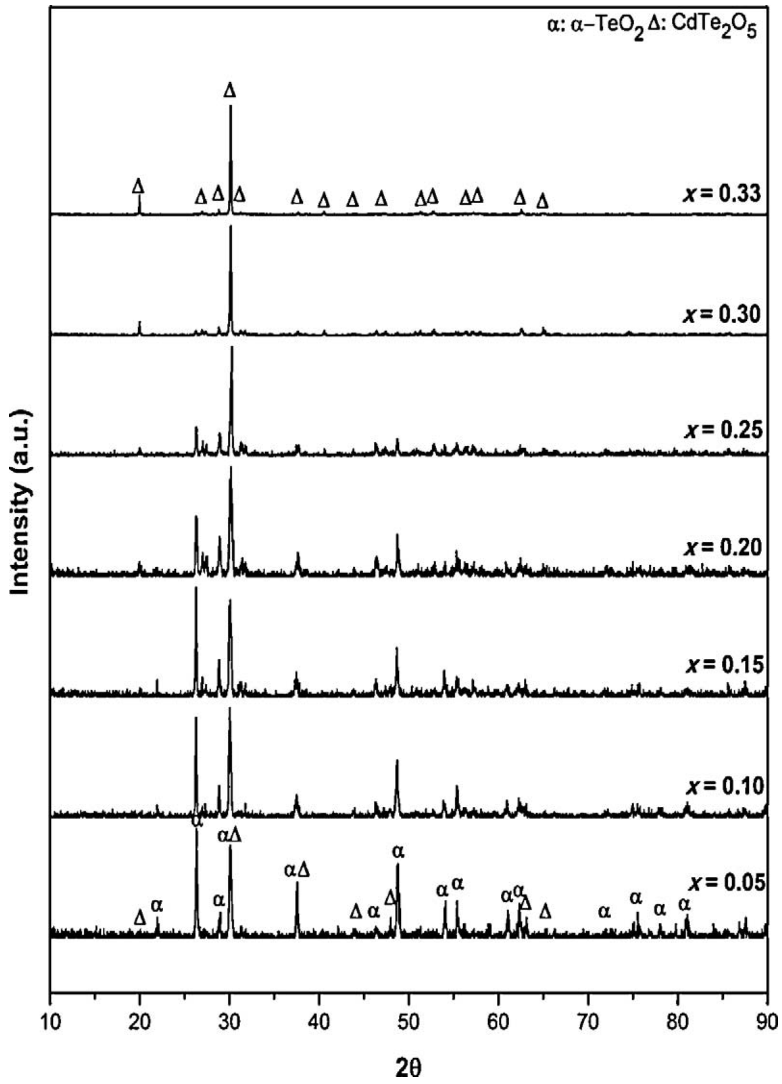

Fig. 7. XRD patterns of $(1-x)TeO_2$–$xCdO$ samples heat-treated at 550 °C for 24 h, where x varies between 0.05 and 0.33, in molar ratio.

towards the eutectic composition with the changing CdO content for the heat-treated samples. Endothermic peaks corresponding to the eutectic and liquidus reactions obtained for the heat-treated samples were detected almost at the same temperature values with the as-cast samples. In the literature, the eutectic temperature for the TeO_2–$CdTe_2O_5$ binary system was reported as 630 °C for 18 mol% CdO by Robertson et al.,[11] however the eutectic temperature was detected at slightly higher temperatures (638 ± 4 °C) under our experimental conditions with repeated thermal analysis.

XRD analyses were carried out with the heat-treated samples at 550 °C to identify the crystalline phases present in the final structure and the XRD patterns of the fully crystalline samples are given in Fig. 7. As it is seen from Fig. 7, when the crystallization was fully achieved, the XRD patterns of the heat-treated samples showed the crystallization of α-TeO_2 and $CdTe_2O_5$ phases. With increasing CdO content, α-TeO_2 peak intensities showed a decrease, while $CdTe_2O_5$ became more pronounced and for *TC*33 sample, only $CdTe_2O_5$ phase was present in the structure. The obtained XRD results show good agreement with the literature.[11]

SEM investigations were conducted on heat-treated samples in order to identify the morphology of the final microstructures when the crystallization was completed. Fig. 8 represents the SEM micrographs of $(1-x)TeO_2$–$xCdO$ samples for different magnifications. Fig. 8a is the representative SEM micrograph of the *TC*5 sample revealing the layered rod-shaped crystallites on the general structure. SEM micrograph of *TC*10 sample (Fig. 8b) showed centro-symmetric rod-like crystallites. Fig. 8c, the SEM micrograph of *TC*15 sample, revealed the degradation of rod-like crystallites and the formation of fine crystallites. With the increasing CdO content, the SEM micrographs of *TC*20, *TC*25, *TC*30 and *TC*33 samples (Fig. 8d–g) showed the formation of triangular plane-like crystallites with different orientations. In general, SEM micrographs of heat-treated samples revealed the presence of α-TeO_2 and $CdTe_2O_5$ crystallites and it was observed that with increasing CdO content, the rod-like crystallites converted into triangular plane-like structures.

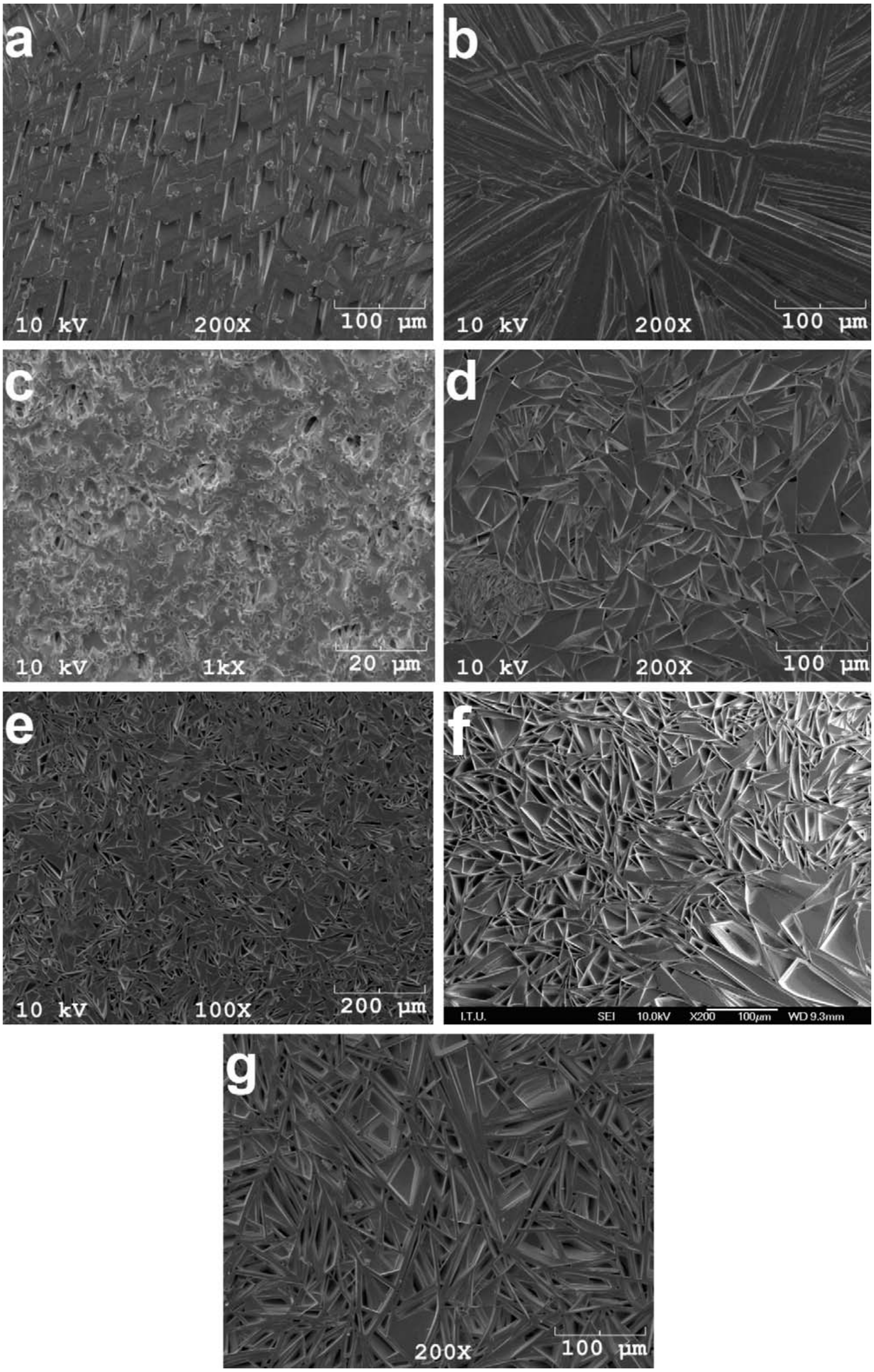

Fig. 8. SEM micrographs of the $(1-x)TeO_2$–$xCdO$ samples heat-treated at 550 °C, where x = (a) 0.05, (b) 0.10, (c) 0.15, (d) 0.20, (e) 0.25, (f) 0.30, (g) 0.33, in molar ratio.

4. Conclusions

The phase equilibria and the glass formation range of the TeO_2-rich part of the $(1-x)TeO_2$–$xCdO$ (where $x = 0.05$–0.33 in molar ratio) system were investigated by using DTA, XRD and SEM techniques. The glass forming region of the system was determined as $0.05 \le x < 0.15$ and the sample containing 10 mol% CdO showed the highest glass stability. Crystallization behavior of the TeO_2–CdO glasses was investigated and the first crystallized phase from the glass matrix was found to be the δ-TeO_2 at around 335 °C and the formation of γ-TeO_2 phase was observed at about 370 °C. The transformation of metastable δ-TeO_2 into stable α-TeO_2 phase and the formation of $CdTe_2O_5$ phase were detected at around 425 °C and metastable γ-TeO_2 phase was transformed into α-TeO_2 phase when the thermal equilibrium was achieved at 550 °C. In order to obtain thermal stability of the system, as-cast samples were heat-treated above all crystallization reaction temperatures at 550 °C for 24 h. A binary eutectic: liquid → $TeO_2 + CdTe_2O_5$ was detected at 638 ± 4 °C for the heat-treated samples. Based on the determined XRD and SEM investigations, α-TeO_2 and $CdTe_2O_5$ crystalline phases were found to be present in the final structure when the final crystallization was achieved. SEM micrographs of TeO_2–CdO samples heat-treated at 550 °C revealed the presence of α-TeO_2 and $CdTe_2O_5$ crystallites. It was observed that with increasing CdO content, the rod-like crystallites converted into triangular plane-like crystallites. Although a similar phase equilibria behavior was obtained with the literature, in the present study the crystallization behavior of the TeO_2–CdO glasses and microstructural characterization of the TeO_2–$CdTe_2O_5$ system was realized for the first time to our knowledge in the literature.

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