



Experimental Phase Studies in the $\text{TeO}_2\text{-CdO}$ System

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Abstract

In the present study, phase equilibrium in the $\text{TeO}_2\text{-CdO}$ system has been investigated. Different compositions of $(1-x)\text{TeO}_2\text{-xCdO}$, where $x = 0.10, 0.20, 0.25, 0.30$ and 0.40 in molar ratio were prepared. The samples waited at 750°C in a platinum crucible for 30 minutes and then quenched in a water bath. DTA studies performed on as-cast samples. According to the DTA results, all samples were heat-treated at 550°C for 24 hours to obtain phase equilibrium. XRD and SEM/EDS studies were performed on the crystallized samples for microstructural analysis.

Keywords: Tellurite glasses, $\text{TeO}_2\text{-CdO}$ system, Phase equilibrium

EKSPERYMENTALNE BADANIA FAZOWE W UKŁADZIE $\text{TeO}_2\text{-CdO}$

W prezentowanej pracy zbadano równowagę fazową w układzie $\text{TeO}_2\text{-CdO}$. Przygotowano różne składy $(1-x)\text{TeO}_2\text{-xCdO}$, gdzie $x = 0,10, 0,20, 0,25, 0,30$ i $0,40$ mol.%. Próbkę przetrzymywano w 750°C w tyglu platynowym przez 30 min., a następnie szybko chłodzono w kąpeli wodnej. Badania DTA przeprowadzono na świeżo wytopionych próbkach. Zgodnie z wynikami DTA, wszystkie próbki wygrzewano w 550°C przez 24 h, aby uzyskać stan równowagi fazowej. Badania XRD i SEM/EDS przeprowadzono na wykrystalizowanych próbkach w przypadku analizy mikrostrukturalnej.

Słowa kluczowe: szkła tellurytowe, układ $\text{TeO}_2\text{-CdO}$, równowaga fazowa

1. Introduction

Recently, tellurite glasses have received considerable attention for their potential use in fibre optics, laser hosts and nonlinear optical materials. Comparing with silicate, borate and phosphate glasses, tellurite glasses have preferable properties, such as low-phonon energy, high refractive index, high dielectric constant, good corrosion resistance, thermal and chemical stability [1-4].

TeO_2 , as a pure oxide, does not have glass forming ability under normal quenching conditions, therefore addition of a network modifier such as heavy metal oxides increase the glass forming tendency. As part of a systematic study on the tellurite glasses, WO_3 was selected as a network modifier. The addition of CdO to tungsten tellurite glasses shortens the solidification time and increases the thermal stability due to the formation of covalent bonds in the glassy matrix [5]. According to these favourable properties, the effect of CdO content on the phase equilibrium of $\text{TeO}_2\text{-CdO}$ binary system was investigated.

$\text{TeO}_2\text{-CdO}$ binary system was studied before by Robertson *et al.* [6]. He proposed that cadmium di-tellurite (CdTe_2O_5), cadmium mono-tellurite ($\text{CdO}\cdot\text{TeO}_2$) and a complex phase, namely $8\text{CdO}\cdot 9\text{TeO}_2$ exist in the binary phase diagram [6]. However, there is an uncertainty on the founded

$8\text{CdO}\cdot 9\text{TeO}_2$ crystalline phase, near the 50 mol.% region. Therefore, in this study the binary system was studied up to 40 % CdO in molar ratio to clarify the uncertain crystalline phases and improve the existing phase diagram. The present study, which is a part of $\text{TeO}_2\text{-WO}_3\text{-CdO}$ phase equilibrium investigation, aims to determine the phase equilibrium of $\text{TeO}_2\text{-CdO}$ sub-system by applying thermal and microstructural characterization techniques.

2. Experimental

Five different samples of $\text{TeO}_2\text{-CdO}$ binary system with the compositions of $(1-x)\text{TeO}_2\text{-xCdO}$ ($x = 0.10, 0.20, 0.25, 0.30$ and 0.40 in molar ratio) were prepared by using reagent grade of TeO_2 (99.99 % purity, Alfa Aesar Company) and CdO (99.9 % purity, Chempur). The powder batches of 5 g size were melted in a platinum crucible with a close lid at 750°C for 30 minutes. The molten samples quenched in a water bath and thermal characterization experiments were carried out by using differential thermal analysis (DTA) technique. According to the DTA results, as-cast samples were heat treated at 550°C for 24 hours and in order to obtain thermal equilibrium of the system, thermal analyses were repeated with heat-treated samples. Thermal characterization experiments were carried out in a Perkin Elmer™ Diamond TG/

DTA to determine the crystallization, eutectic and liquidus temperatures. The DTA scans were recorded by using 25 mg of powdered samples, with a heating rate of 10 K/min from room temperature to 750°C in a platinum crucible.

X-ray diffraction (XRD) analyses were carried out on heat-treated samples to determine the crystalline phases, and scanning electron microscopy (SEM) studies were conducted for microstructural characterization. The x-ray diffraction investigations were carried out with powdered samples in a Bruker™ D8 Advanced Series powder diffractometer. All diffraction patterns were recorded using Cu K α radiation in the 2 θ range from 10° to 90°. The Joint Committee on Powder Diffraction Standards (JCPDS) data files were used to determine the crystallized phases by comparing the peak positions and intensities. SEM investigations were conducted with fully crystallized gold-coated bulk samples in a JEOL™ Model JSM 5410, operated at 10 kV and linked with Noran 2100 Freedom energy dispersive spectrometer (EDS) attachment. For all samples, surface SEM micrographs were taken in the secondary electron imaging (SEM/SEI) mode.

3. Results and discussion

3.1. Thermal Investigations

The DTA curves of 0.90TeO₂-0.10CdO, 0.80TeO₂-0.20CdO, 0.75TeO₂-0.25CdO, 0.70TeO₂-0.30CdO and 0.60TeO₂-0.40CdO samples scanned at a heating rate of 10 K/min up to 750°C are displayed in Fig. 1.

DTA scans show exothermic peaks corresponding to the crystallization of phases and endothermic peaks related to the eutectic and liquidus temperatures. The crystallization onset and peak (T_c/T_p), eutectic onset and peak (T_e/T_m), liquidus peak (T_l) temperature values were given in Table 1.

Heterogeneous as-cast samples with transparent and non-transparent regions were obtained, indicating a partial glassy formation. Therefore, weak exothermic peaks were observed on the DTA curves according to the residual glassy regions in these samples. Ongoing studies are still in progress in order to clarify this partial glassy formation. For $x = 0.10$ and $x = 0.20$ compositions, exothermic peak onset temperatures were found at 401 and 406°C, respectively, while for $x = 0.25$ and $x = 0.30$ compositions no exothermic peak was observed. A weak crystallization reaction for $x = 0.40$ composition was detected with the exothermic reaction onset temperature at 484°C, probably indicating the transformation of an unstable phase to a stable form.

For all samples, where $x \leq 0.30$ a similar endothermic peak was observed, indicating the first eutectic reaction of the TeO₂-CdO binary phase diagram. The eutectic peak onset temperature was observed at $636 \pm 1^\circ\text{C}$, while the peak temperature was found at $642 \pm 2^\circ\text{C}$.

For $x = 0.40$ composition, with increasing CdO content, one endothermic peak was found at higher temperatures (T_e : 690°C), corresponding to the second eutectic reaction of the TeO₂-CdO binary system.

In the TeO₂-CdO phase diagram obtained by Robertson *et al.*, two eutectic reactions were also determined taking place at 18 mol.% CdO and 35.5 mol.% CdO with the onset values $630 \pm 3^\circ\text{C}$ and $690 \pm 3^\circ\text{C}$, respectively [6].

For $x = 0.10$ composition a second endothermic peak was determined at 695°C, representing the liquidus temperature. The liquidus peak was not detected for $x = 0.20$ composition, since its closeness to the first eutectic composition proposed by Robertson *et al.* [6].

For $x = 0.25$ and $x = 0.30$, a second endothermic peak was determined at 671 and 692°C, respectively, representing the liquidus temperatures for the first hyper-eutectic region of the TeO₂-CdO phase diagram, which is in agreement with the literature. The liquidus peak was not detected for $x = 0.40$ composition, since this composition is close to the second eutectic composition.

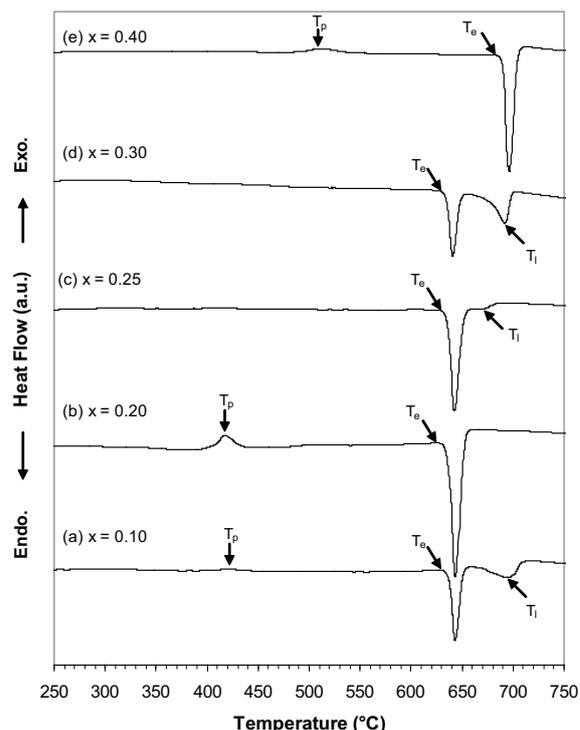


Fig. 1. DTA curves of $(1-x)\text{TeO}_2-x\text{CdO}$ as-cast samples, where: a) $x = 0.10$, b) $x = 0.20$, c) $x = 0.25$, d) $x = 0.30$ and e) $x = 0.40$ in molar ratio.

Table 1. Values of crystallization onset, T_c , crystallization peak, T_p , eutectic onset, T_e , eutectic peak, T_m , liquidus peak, T_l , temperatures ($^\circ\text{C}$) of the $(1-x)\text{TeO}_2+x\text{CdO}$ samples.

Samples	T_c/T_p	T_e/T_m	T_l
$x = 0.10$	401/422	637/642	695
$x = 0.20$	406/418	637/644	
$x = 0.25$		636/642	671
$x = 0.30$		635/641	692
$x = 0.40$	484/512	690/696	

3.2. Microstructural characterization

On the basis of the DTA results, XRD and SEM studies were conducted on heat-treated samples for phase and microstructural characterization after thermal equilibrium achieved. The XRD patterns of the fully crystallized samples are given in Fig. 2.

According to the XRD analyses, up to $x = 0.30$ composition the structure was composed of α -TeO₂ (paratellurite) and

CdTe_2O_5 crystalline phases. With increasing CdO content up to $x = 0.30$ composition, $\alpha\text{-TeO}_2$ (paratellurite) peak intensities decrease and the CdTe_2O_5 becomes the dominant crystalline phase in the system.

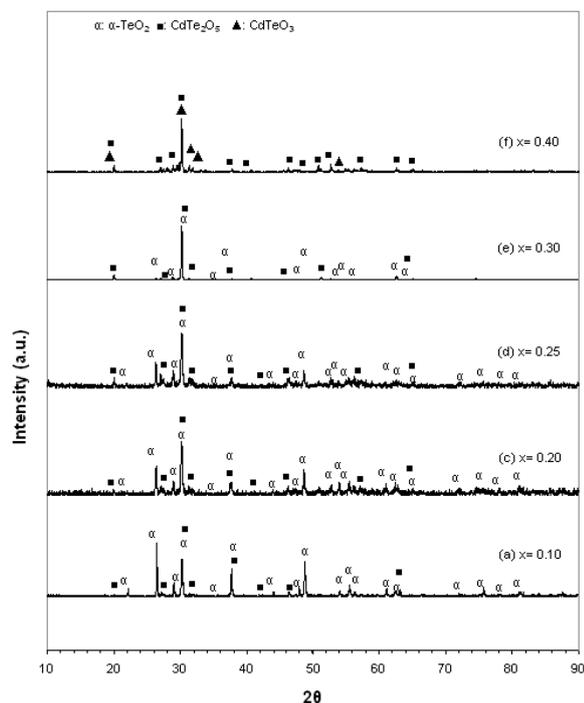


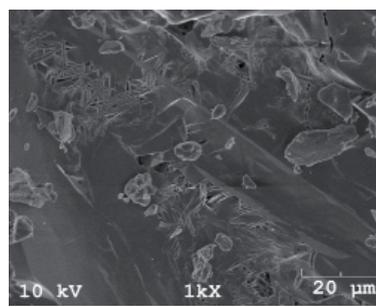
Fig. 2. X-ray diffraction patterns of $(1-x)\text{TeO}_2-x\text{CdO}$ samples heat-treated at 550°C for 24 hours: a) $x = 0.10$, b) $x = 0.20$, c) $x = 0.25$, d) $x = 0.30$ and e) $x = 0.40$.

For $x = 0.40$ composition, the d -values of the peaks matched the card values of CdTe_2O_5 and CdTeO_3 . However, Robertson *et al.* [6] proposed a complex phase, namely $8\text{CdO}\cdot 9\text{TeO}_2$, for this composition with the existing cadmium di-tellurite (CdTe_2O_5). On the contrary, as a result of XRD analysis realized with $x = 0.40$ composition, it was determined that the $8\text{CdO}\cdot 9\text{TeO}_2$ phase does not exist in the $\text{TeO}_2\text{-CdO}$ binary system.

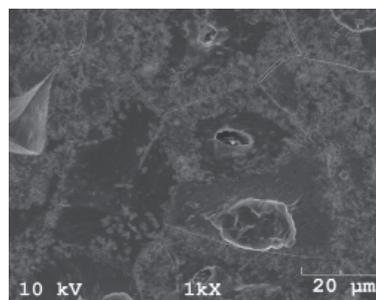
SEM investigations were performed on the crystallized $(1-x)\text{TeO}_2-x\text{CdO}$ samples in order to identify the morphology of the crystalline phases. Fig. 3a represents the SEM micrograph of the $0.90\text{TeO}_2\text{-}0.10\text{CdO}$ sample, which reveals the presence of two different crystal formations also detected in the XRD scans. Elongated rod-like crystallites align throughout the whole structure, which is considered to be $\alpha\text{-TeO}_2$ crystals exist together with the precipitation of needle-like secondary crystallites belong to CdTe_2O_5 which was also reported by Tatar *et al.* for the $0.85\text{TeO}_2\text{-}0.15\text{CdF}_2$ sample [3].

For the $0.80\text{TeO}_2\text{-}0.20\text{CdO}$ sample, rod-like crystallites could not be observed and smaller needle-like crystallites precipitate on the surface as shown in Fig. 3b. With increasing CdO content, SEM micrograph of the $0.70\text{TeO}_2\text{-}0.30\text{CdO}$ sample, reveals that the needle-like primary crystalline phase forms the matrix (CdTe_2O_5 phase) and a secondary crystalline phase present in the structure as rod-like crystallites ($\alpha\text{-TeO}_2$).

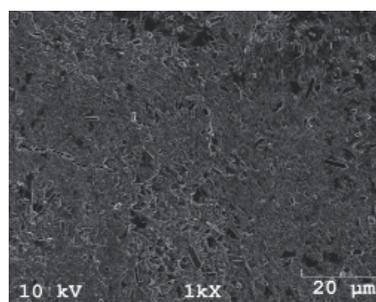
For $0.60\text{TeO}_2\text{-}0.40\text{CdO}$ sample, the structure composed of small needle-like crystallites belong to CdTe_2O_5 phase with stripe-like crystallites considered to be CdTeO_3 also detected by XRD analysis (Fig. 3d).



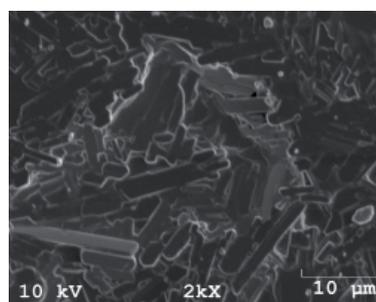
a)



b)



c)



d)

Fig. 3. SEM micrographs of $(1-x)\text{TeO}_2-x\text{CdO}$ samples, where: a) $x = 0.10$, b) $x = 0.20$, c) $x = 0.30$ and d) $x = 0.40$.

4. Conclusions

Different samples of $\text{TeO}_2\text{-CdO}$ binary system, with the compositions of $(1-x)\text{TeO}_2-x\text{CdO}$, ($x = 0.10, 0.20, 0.25, 0.30$ and 0.40 in molar ratio) were studied by DTA, XRD and SEM techniques to obtain the phase equilibrium by investigating the thermal and microstructural behaviour of the system. Crystallization or transformation of the crystalline phases and the melting temperatures were determined by means of differential thermal analysis technique. Two binary eutectic reactions were determined with the onset values at $636 \pm 1^\circ\text{C}$ and 690°C , which is in agreement with the literature. Based on the determined XRD patterns, for $x \leq 0.30$ composition, $\alpha\text{-TeO}_2$ (paratellurite) and CdTe_2O_5 crystalline phases were found.

For $x = 0.40$ composition, α -TeO₂ phase was not detected, while a crystalline phase namely, cadmium mono-tellurite (CdTeO₃) was formed with the existing cadmium di-tellurite (CdTe₂O₅). The complex and uncertain 8CdO×9TeO₂ phase reported in the literature was not detected for this composition. SEM investigations revealed different microstructures which are rod-like crystallites considered belong to α -TeO₂, needle-like crystallites belong to CdTe₂O₅ and stripe-like crystallites considered to be CdTeO₃.

Acknowledgements

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