A Review of Scanning Electron Microscopy Investigations in Tellurite Glass Systems

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Tellurite glasses have recently become technologically and scientifically important in optical communication systems as host materials for optical fibers and amplifiers due to their outstanding properties, such as relatively low phonon energy, high refractive index, high dielectric constant, good infrared transmittance, low glass transition and melting temperature, thermal and chemical stability and high crystallization resistance. In order to develop tellurite glasses and glass ceramics for optical applications, it is important to control the crystallization process and understand their thermal, phase and microstructural behavior. Therefore, a detailed microstructural characterization of tellurite glasses is crucial to obtain a desired property or behavior. In this mini-review, it is proposed to investigate the crystallization and phase separation behavior in different binary and ternary tellurite glasses by applying systematical thermal, phase and microstructural characterizations. The crystallization behavior of glasses, morphologies of the crystallized phases and phase separation process in glass systems were identified using in-situ and ex-situ X-ray diffraction (XRD), scanning electron microscopy and energy dispersive X-ray spectrometry (SEM/EDS) analysis.

Keywords: tellurite glasses; crystallization behavior; phase separation; microstructural characterization; scanning electron microscopy; energy dispersive X-ray spectrometry

1. Introduction

Optical communication is one of today's cutting-edge research topics due to the innovations they brought to scientific and technological applications by allowing the transmission of much bigger amount of information than the classic transmission media such as radio waves or copper wires at lower costs for longer distances [1]. Optical communication systems basically consist of optical fibers and amplifiers [2-3]. The development of optical fibers and amplifiers is a complex task due to the problems associated to their design and production, and due to the absence of materials having all the required properties [1]. Glasses are ideal materials for optical communication systems due to their advantageous properties [4]. Therefore, until today silicate, borate and phosphate glasses were preferred as glass matrices in optical communication systems [5,6]. Tellurite glasses have recently drawn considerable attention as promising matrices for optical communication systems due to their superior properties, such as relatively low-phonon energy, high refractive index, high dielectric constant, good infrared transmissivity, low glass transition and melting temperature, thermal and chemical stability and high devitrification resistance [6-14].

Tellurium dioxide (TeO₂) is a conditional glass former which does not have glass forming ability under normal quenching conditions without the addition of a secondary component. Therefore, secondary components, such as heavy metal oxides, alkalis or halogens increase its forming ability [6-14]. Addition of WO₃, as a network modifier or an intermediate oxide, to tellurite glasses provides several advantageous properties, such as doping with rare earth elements in a wide range, modifying the composition by a third, fourth, and even fifth component, enhancing the chemical stability and devitrification resistance. Furthermore, compared to other tellurite glasses, tungsten-tellurite glasses have slightly higher phonon energy and higher glass transition temperature, therefore they can be used at high optical intensities without exposure to thermal damage [6,9,10,13,14]. Addition of CdO, an intermediate oxide, stabilizes the glass structure, increases the dielectric constant and enhances the optical and electrical properties [10,12]. Addition of B₂O₃, a good glass former, enhances the thermal and chemical stability and crystallization resistance [9,15]. Due to these favorable properties, in this mini-review, the binary TeO₂-WO₃, TeO₂-CdO and TeO₂-B₂O₃ and ternary TeO₂-WO₃-CdO and TeO₂-WO₃-B₂O₃ tellurite glass systems were investigated.

In order to use tellurite glasses in optical communication systems, it is crucial to determine their crystallization behavior by considering the thermal, phase and microstructural properties. Scanning electron microscopy is an important microstructural characterization technique which elucidates the morphology of the crystalline phases. In this work, it was aimed to review the scanning electron microscopy investigations for the microstructural characterization of crystallization behavior and phase separation process in different tellurite-based glass systems.
2. Materials and Methods

A conventional melt-quenching technique was used to synthesize the glass samples by using high purity powders of the constituent oxides (TeO$_2$ 99.99% purity Alfa Aesar Company, WO$_3$ 99.8% purity Alfa Aesar Company, CdO 99.95% purity Alfa Aesar Company and H$_2$BO$_3$ 99.5% purity Sigma-Aldrich Company). Thoroughly mixed powders were melted in a platinum crucible with a closed lid at 750-850 °C for 30 minutes in an electrical furnace and quenched in water bath.

Thermal behavior of the glass samples was investigated by applying differential thermal analysis (DTA) and differential scanning calorimetry (DSC) analysis in a Perkin Elmer™ Diamond TG/DTA and Netzsch DSC 204 F1, respectively. A constant sample weight of 25 ± 1 mg was used under flowing argon gas with a heating rate of 10 °C/min. Thermal analysis of the samples was carried out to determine the glass transition onset ($T_g$) and crystallization onset and peak ($T_c/T_p$) temperatures.

To recognize the crystallization behavior, the glass samples were heat-treated above each exothermic reaction onset temperature and the thermal equilibrium of the existing phases was obtained. Characterization of the crystalline phases was realized by running in-situ and ex-situ X-ray diffraction, scanning electron microscopy and energy dispersive X-ray spectrometry (SEM/EDS) analyses. Ex-situ XRD investigations were carried out with heat-treated samples in a Bruker™ D8 Advanced Series powder diffractometer using Cu K$_{\alpha}$ radiation in the 2θ range from 10° to 90°. In-situ XRD measurements were realized with a Philips X'pert MRD (Cu K$_{\alpha}$ radiation) fitted with a high temperature furnace (Anton-Parr DHi5900). The heating rate was 10 °C/min and each pattern was recorded after an annealing time of 10 minutes at the chosen temperatures, in the 2θ range from 10° to 90°. 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 experiments was conducted with gold or platinum coated bulk samples in JEOL™ Model JSM 5410 and JEOL™ Model JSM 7000F scanning electron microscopes (SEM) linked with Noran 2100 Freedom and Oxford Inca energy dispersive X-ray spectrometer (EDS) attachments, respectively.

3. SEM Investigations of crystallization behavior in tellurite glass systems

TeO$_2$ has two polymorphs at ambient conditions: tetragonal $\alpha$-TeO$_2$ (paratellurite) and orthorhombic $\beta$-TeO$_2$ (tellurite) and two metastable polymorphs which are obtained in the doped TeO$_2$ glasses depending on the amount of the added component: orthorhombic $\gamma$-TeO$_2$ and cubic $\delta$-TeO$_2$[6,11]. In this section, phase transformation of TeO$_2$ was studied by investigating the crystallization behavior of different binary and ternary tellurite glass systems.

3.1 TeO$_2$-WO$_3$ glass system

Crystallization behavior of the (1-x)TeO$_2$-xWO$_3$ glasses, which was found to have a glass formation range in our previous study between 4-35 mol % WO$_3$[14], was investigated with the selected 0.90TeO$_2$-0.10WO$_3$, 0.85TeO$_2$–0.15WO$_3$ and 0.80TeO$_2$–0.20WO$_3$ glass samples by applying DSC, XRD and SEM analysis.

To recognize the crystallization behavior of the as-cast samples, DSC analysis was carried out and the crystallization onset temperatures of the first exothermic reactions were determined. According to the thermal analysis results, 410 °C, 430°C and 490 °C were selected as annealing temperatures for 0.90TeO$_2$–0.10WO$_3$, 0.85TeO$_2$–0.15WO$_3$ and 0.80TeO$_2$–0.20WO$_3$ samples, respectively. As-cast samples were heat-treated above the first exothermic reaction onset temperatures for 24 hours to investigate the phases crystallized from the glass matrix. XRD patterns of the as-cast and heat-treated samples are given in Fig. 1.

XRD patterns of the as-cast samples revealed no detectable peaks, proving the amorphous structure. As shown in Fig. 1a-b, XRD analysis of 0.90TeO$_2$–0.10WO$_3$ sample heat-treated at 410 °C and 0.85TeO$_2$–0.15WO$_3$ sample heat-treated at 430 °C showed the crystallization of $\alpha$-TeO$_2$ and $\gamma$-TeO$_2$ phases. As shown in Fig. 1c, XRD analysis of 0.80TeO$_2$–0.20WO$_3$ sample heat-treated at 490 °C showed the presence of $\alpha$-TeO$_2$ and WO$_3$ phases.

SEM analyses were conducted on the heat-treated samples for the microstructural investigation of the crystallization behavior in the TeO$_2$-WO$_3$ glass system, and surface and cross-sectional SEM micrographs are shown in Fig. 2.

SEM micrograph of the 0.90TeO$_2$–0.10WO$_3$ sample heat-treated at 410 °C taken from the surface (Fig. 2a) exhibits the presence of differently oriented dendritic leaf-like crystallites and the cross-sectional micrograph of this sample (Fig.2b) shows a typical amorphous structure without any crystallization on the bulk. The surface SEM micrograph of the 0.85TeO$_2$–0.15WO$_3$ sample (Fig. 2c) reveals differently oriented dendritic lamellar crystallites, while the cross-sectional SEM micrograph of the sample (Fig. 2d) shows typical amorphous structure on the bulk. As shown in Fig. 2e-f, the representative SEM micrographs taken from the surface and cross-section of the 0.80TeO$_2$–0.20WO$_3$ sample heat treated at 490 °C shows that rod-like crystallites are present throughout the surface but they do not diffuse into the bulk. Based on the SEM investigations, it was determined for all samples that the crystallization occurred on the surface and the crystallites did not diffuse into the bulk structure proving the surface crystallization mechanism.
Microstructural investigation of the phases in thermal equilibrium in the $(1-x)\text{TeO}_2-x\text{WO}_3$ system was realized with different samples. According to the thermal analysis results, as-cast samples were heat-treated above all crystallization peak temperatures at 550 °C for 24 hours. To identify the crystalline phases present in the final structure, XRD analyses were carried out on heat-treated samples and XRD patterns of the fully crystalline samples showed that $\alpha$-TeO$_2$ and WO$_3$ phases were present in the final structure. SEM investigations were performed on heat-treated samples in order to identify the morphology of the final microstructures when the crystallization was completed. Thusly, microstructural morphology of the TeO$_2$–WO$_3$ system was investigated according to the increasing WO$_3$ content. SEM micrographs of the $(1-x)\text{TeO}_2-x\text{WO}_3$ samples heat-treated at 550 °C are given in Fig. 3.
Fig. 3 SEM micrographs of the (1-\(x\))TeO\(_2\)-\(x\)WO\(_3\) samples heat-treated at 550 °C for 24 hours, where \(x\) = a) 0.03, b) 0.10, c) 0.20, d) 0.25, e) 0.30, f) 0.35, g) 0.40, h) 0.60, in molar ratio (Reprinted from reference [14] with permission from Elsevier).

Fig. 3a shows the representative SEM micrograph of the heat-treated 0.97TeO\(_2\)-0.03WO\(_3\) sample revealing grain-like crystallites (40–50 \(\mu\)m size) in the general structure with the presence of a secondary phase precipitated along the grain boundaries. EDS spectra taken from the grains and grain boundaries showed that the WO\(_3\) content is four times higher along the grain boundaries than the grains. As seen in the SEM micrograph of 0.90TeO\(_2\)-0.10WO\(_3\) sample (Fig. 3b), a strong decrease in the size of the grains (1–1.5 \(\mu\)m size) was detected with the presence of a secondary phase precipitated along the grain boundaries. SEM micrographs of the samples (\(x\) = 0.20, 0.25 and 0.30 in molar ratio) given in Fig. 3c-d-e showed the degradation of grain-like crystallites and the formation of centrosymmetric leaf-like crystallites which show dendritic rod-like structure in various orientations. The representative SEM micrograph of the 0.65TeO\(_2\)-0.35WO\(_3\) sample revealed the degradation of the centrosymmetric leaf-like structures and the regeneration of the grain-like crystallites (Fig. 3f). As seen in Fig. 3g, small polygonal crystallites were found to exist throughout the structure, ranging approximately between 2-4\(\mu\)m in size for the 0.60TeO\(_2\)-0.40WO\(_3\) sample. For the 0.40TeO\(_2\)-0.60WO\(_3\) sample, SEM micrograph given in Fig. 3h revealed small orthogonal crystallites in the structure, having crystal sizes of about 0.5–2\(\mu\)m. SEM micrographs of the TeO\(_2\)-WO\(_3\) samples heat-treated at 550 °C revealed the presence of primary grains belonging to the \(\alpha\)-TeO\(_2\) phase and the formation of WO\(_3\) crystallites. It was observed that with increasing WO\(_3\) content, the granular shape of the \(\alpha\)-TeO\(_2\) crystalline phase converted into a leaf-like structure. Likewise, the precipitated WO\(_3\) crystalline phase along the grain boundaries turned into orthogonal crystallites and spread throughout the structure with increasing WO\(_3\) content.

3.2 TeO\(_2\)-CdO glass system
Crystallization behavior of the (1-\(x\))TeO\(_2\)-\(x\)CdO system, which was found to have a narrow glass formation range (0.05 ≤ \(x\) < 0.15 mol % CdO) [12], was investigated with the selected 0.90TeO\(_2\)-0.10CdO sample. DTA result of the as-cast 0.90TeO\(_2\)-0.10CdO sample revealed a glass transition reaction (\(T_g\)) at 303 °C and four exothermic reactions with the onset temperatures at 327, 358, 410 and 495 °C, respectively. To achieve the thermal equilibrium of the crystalline phases, as-cast 0.90TeO\(_2\)-0.10CdO sample was heat-treated above each exothermic onset temperature for 24 hours (at 335, 370, 425 and 550 °C) and XRD analyses were realized to identify the crystallized phases (Fig. 4).
Fig. 4 XRD patterns of the as-cast and heat-treated 0.90TeO₂–0.10CdO sample (Reprinted from reference [12] with permission from Elsevier).

XRD pattern of the as-cast sample confirmed the amorphous nature of the glass sample. According to the XRD investigations of the 0.90TeO₂–0.10CdO sample, it was found that for TeO₂–CdO glass system, δ-TeO₂ phase was crystallized from the glass matrix at around 335 °C, the formation of γ-TeO₂ phase was observed at about 370 °C and the transformation of δ-TeO₂ phase into α-TeO₂ was observed at around 425 °C. At 550 °C, γ-TeO₂ phase was transformed into α-TeO₂ phase, therefore α-TeO₂ and CdTe₂O₅ phases were found to be present in the system when the thermal equilibrium was achieved.

In order to identify the morphology of the crystallized phases in the TeO₂–CdO glass system, SEM investigations were conducted on as-cast and heat-treated (at 335, 370, 425 and 550 °C) 0.90TeO₂–0.10CdO sample and the SEM micrographs are given in Fig. 5a-e.

Fig. 5 SEM images of 0.90TeO₂–0.10CdO 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 (Reprinted from reference [12] with permission from Elsevier).

SEM micrograph of the as-cast 0.90TeO₂–0.10CdO sample (see Fig. 5a) revealed no crystallization, proving the amorphous nature of the sample. As can be seen from Fig. 5b, the micrograph of the 0.90TeO₂–0.10CdO sample heat-treated at 335 °C shows grain-like crystallites on the surface revealing the formation of δ-TeO₂ phase from the glassy matrix. The SEM micrograph of the sample heat-treated at 370 °C (see Fig. 5c) showed that the grain-like crystallites corresponding to the δ-TeO₂ phase are still present in the structure and worm-like crystallites related to the γ-TeO₂ phase were found to crystallize in the structure. SEM image of the sample heat-treated at 425 °C (Fig. 5d) showed that
the grain-like crystallites which belong to the $\delta$-TeO$_2$ phase are no longer present in the structure, $\gamma$-TeO$_2$ phase is still present as worm-like crystallites and large grain-like crystallites were started to form in the structure due to the formation of the CdTe$_2$O$_5$ phase. SEM micrograph of the sample heat-treated at 550 °C (Fig. 5e) revealed that grain-like crystallization corresponding to the $\alpha$-TeO$_2$ and CdTe$_2$O$_5$ phases occurred in the general structure.

3.3 TeO$_2$-WO$_3$-CdO glass system

Crystallization behavior of the TeO$_2$–WO$_3$–CdO glasses was investigated with the selected 0.90TeO$_2$-0.05WO$_3$-0.05CdO (in molar ratio) sample by applying thermal, phase and microstructural characterizations. DTA analysis of the as-cast sample showed an endothermic change at 313 °C corresponding to the glass transition temperature and several exothermic peaks indicating different crystallization reactions. To characterize the crystallization reactions observed in thermal analysis, as-cast 0.90TeO$_2$–0.05WO$_3$–0.05CdO sample was heat-treated above the crystallization reaction onset temperatures for 24 hours (at 365, 435 and 550 °C) and XRD analyses were realized to identify the crystallized phases. XRD analysis results of the as-cast and heat-treated samples are given in Fig. 6.

As can be seen from Fig. 6, XRD patterns of the as-cast sample revealed no detectable peaks, proving the amorphous structure. XRD result of the sample heat-treated at 365 °C revealed the formation of metastable $\delta$-TeO$_2$ phase. The observed peak positions of the sample heat-treated at 435 °C matched with the metastable $\gamma$-TeO$_2$ and $\delta$-TeO$_2$ phases.

At 550 °C, when the thermal equilibrium was achieved, $\delta$-TeO$_2$ and $\gamma$-TeO$_2$ phases were transformed into stable $\alpha$-TeO$_2$ phase and $\alpha$-TeO$_2$ and CdWO$_4$ phases were found to be present in the structure.

![Fig. 6 XRD patterns of the as-cast and heat-treated 0.90TeO$_2$–0.05WO$_3$–0.05CdO sample.](image)

To have a deep understanding on the morphology of the as-cast and heat-treated samples, SEM/EDS investigations were conducted. SEM micrographs taken from the outer surface of the 0.90TeO$_2$–0.05WO$_3$–0.05CdO sample are shown in Fig. 7.

Fig. 7a shows that no crystallization occurs in the as-cast 0.90TeO$_2$–0.05WO$_3$–0.05CdO sample, proving the amorphous nature. As can be seen in Fig. 7b, SEM micrograph of the sample heat-treated at 365 °C shows grain-like crystallites on the surface. According to the XRD and SEM analysis results, the grain-like crystallites are thought to be due to the formation of $\delta$-TeO$_2$ phase. SEI micrograph of the sample heat-treated at 550 °C (Fig. 7c) shows the presence of grain-like crystallites in general structure with a white colored secondary phase precipitated along the grain boundaries. By taking the XRD results into account and considering the BEI micrograph (Fig. 7d) and EDS results taken from the sample heat-treated at 550 °C, it was determined that the dark colored grain-like crystallites are rich in TeO$_2$ content and correspond to the $\alpha$-TeO$_2$ phase and white colored crystallites precipitated along the grain boundaries are rich in WO$_3$ and CdO and correspond to the CdWO$_4$ phase.
3.4 TeO₂-WO₃-B₂O₃ glass system

Crystallization behavior of the TeO₂–WO₃–B₂O₃ glasses was investigated with the selected 0.80TeO₂-0.10WO₃-0.10B₂O₃ (in molar ratio) sample by using DSC, in-situ XRD and SEM/EDS analysis.

According to the DSC results, onset temperatures of the exothermic peaks were detected and the analysis temperatures for the in-situ XRD analysis were determined. In-situ XRD patterns of the 0.80TeO₂-0.10WO₃-0.10B₂O₃ sample obtained at different temperatures are shown in Fig. 8.

As can be seen from the in-situ XRD patterns, the as-cast sample revealed no detectable peaks confirming the amorphous structure, while the XRD patterns obtained at 445, 460 and 480 °C showed the presence of γ-TeO₂, α-TeO₂, WO₃ and B₂O₃ crystalline phases. XRD analysis realized at 550 °C showed that only α-TeO₂ and WO₃ crystalline phases were found to exist in the system when the thermal equilibrium was achieved due to the transformation of the metastable γ-TeO₂ phase into stable α-TeO₂ phase with increasing temperature. The reason for not detecting B₂O₃ phase in the XRD scan at 550 °C is thought to be due to its potential melting behavior at elevated temperatures within the structure [9].
For the microstructural characterization of the crystallization behavior studies, SEM/EDS investigations were conducted with the heat-treated samples. SEI and BEI micrographs taken from the 0.80TeO$_2$-0.10WO$_3$-0.10B$_2$O$_3$ sample are shown in Fig. 9.

Secondary electron micrograph of the 0.80TeO$_2$-0.10WO$_3$-0.10B$_2$O$_3$ sample heat-treated at 445 °C (Fig. 9a) showed the presence of a network-like structure constituting the general matrix and dendritic rod-like crystallites and irregular dark crystallites on the general matrix. By taking the in-situ XRD results into account and considering the BEI micrograph (Fig. 9b) and EDS analysis result, it was found that the network-like structure forming the general matrix correspond to the formation of $\alpha$-TeO$_2$ and WO$_3$ crystalline phases (82.12 at.% Te and 17.88 at.% W). The rod-like crystallites formed on the general matrix were found to be related to the $\gamma$-TeO$_2$ phase (95.97 at.% Te), while the irregular dark crystallites were found to correspond to the B$_2$O$_3$ phase. SEI (Fig. 9c) and BEI (Fig. 9d) micrographs of the sample heat-treated at 460 °C showed the presence of the network-like structure on the background corresponding to the $\alpha$-TeO$_2$ and WO$_3$ phases, dendritic rod-like crystallites on the general matrix related to the $\gamma$-TeO$_2$ phase and dark crystallites corresponding to the B$_2$O$_3$ phase. It was observed that the dark crystallites corresponding to the B$_2$O$_3$ phase became smaller in size but still present in the structure with the increasing temperature. SEI (Fig. 9e) and BEI (Fig. 9f) micrographs of the sample heat-treated at 480 °C revealed the network-like structure related to the formation of $\alpha$-TeO$_2$ and WO$_3$ crystallites and dendritic rod-like crystallites corresponding to the $\gamma$-TeO$_2$ phase. It was observed that the dark crystallites corresponding to the B$_2$O$_3$ phase became smaller in size but still present in the structure with the increasing temperature. SEI (Fig. 9g) and BEI (Fig. 9h) micrographs of the sample heat-treated at 550 °C showed that grain-like crystallites constituted the general matrix with small white crystallites precipitated along the grain boundaries. It was observed that dendritic rod-like crystallites corresponding to the $\gamma$-TeO$_2$ phase and dark crystallites related to the B$_2$O$_3$ phase are no longer present in the structure. According to the EDS analysis taken from the general matrix, it was determined that the grain-like crystallites belong to the $\alpha$-TeO$_2$ phase (89.77 at.% Te and 10.23 at.% W) and WO$_3$ content is almost three times higher along the grain boundaries (71.79 at.% Te and 28.21 at.% W) meaning that the small white crystallites are related to the WO$_3$ phase.
4. SEM Investigations of phase separation behavior in tellurite glass systems

Two glass former containing binary systems show a stable immiscibility gap due to the simultaneous bonding of glass formers in the structure by preserving their own networks because of their chemical incompatibility [15,16]. The triple combinations of the binary systems showing stable immiscibility also exhibit a wide field of phase separation process [6,17]. In this section, phase separation behavior in B$_2$O$_3$ containing binary and ternary tellurite glasses was investigated.

4.1 TeO$_2$-B$_2$O$_3$ glass system

Phase separation process in the TeO$_2$-B$_2$O$_3$ system was investigated with the selected 0.65TeO$_2$-0.35B$_2$O$_3$ (in molar ratio) sample by using DTA, XRD and SEM/EDS analysis.

As-cast sample was obtained having two different regions in macro size: opaque and transparent. According to the thermal analysis, as-cast 0.65TeO$_2$-0.35B$_2$O$_3$ sample was heat-treated above all crystallization peak temperatures at 520 °C in order to obtain the thermal equilibrium. XRD analysis of the heat-treated sample revealed that $\alpha$-TeO$_2$ and B$_2$O$_3$ phases were present in the structure.

Microstructural characterization of the heat-treated sample was realized in order to investigate the morphology of the phase separation process and SEI and BEI micrographs are shown in Fig. 10.

![Fig. 10 SEM micrographs of the 0.65TeO$_2$-0.35B$_2$O$_3$ sample heat-treated at 520 °C for 24 hours, a) SEI x2000, b) SEI x5000, c) BEI x5000.](image)

SEM micrographs of the sample clearly show the presence of two different regions in the general structure proving the phase separation behavior in TeO$_2$–B$_2$O$_3$ glass system. SEI micrographs (Fig. 10a-b) show that grain-like crystallites and cracked smooth structure constituted the general matrix. According to the BEI micrograph and EDS results, it was found that the grain-like crystallites (representing the transparent region of the as-cast sample) correspond to the $\alpha$-TeO$_2$ phase and cracked smooth structure (representing the opaque region of the as-cast sample) is related to the B$_2$O$_3$ phase. Therefore, it was concluded that the transparent region of the sample is rich in TeO$_2$, while the opaque region is rich in B$_2$O$_3$.

4.2 TeO$_2$-WO$_3$-B$_2$O$_3$ glass system

Phase separation behavior in two glass former containing TeO$_2$-WO$_3$-B$_2$O$_3$ system was investigated with the selected 0.20TeO$_2$-0.30WO$_3$-0.50B$_2$O$_3$ (in molar ratio) sample by running thermal, phase and microstructural analysis.

According to the thermal analysis results, as-cast 0.20TeO$_2$-0.30WO$_3$-0.50B$_2$O$_3$ sample was heat-treated above all crystallization peak temperatures at 550 °C for 1 hour. To identify the crystalline phases present in the final structure, XRD analysis was carried out with the heat-treated sample and it was found that $\alpha$-TeO$_2$, WO$_3$ and B$_2$O$_3$ phases were present in the structure.

To have an understanding on the morphology of the phase separation process in the TeO$_2$-WO$_3$-B$_2$O$_3$ system, microstructural characterization of the heat-treated 0.20TeO$_2$-0.30WO$_3$-0.50B$_2$O$_3$ sample was realized and the BEI micrographs are shown in Fig. 11.

As seen from Fig. 11, the BEI micrographs of the heat treated 0.20TeO$_2$-0.30WO$_3$-0.50B$_2$O$_3$ sample showed two different regions: dark and light-colored, proving the phase separation process in TeO$_2$-WO$_3$-B$_2$O$_3$ system. As shown in Fig. 11b, the dark-colored region is composed of grain-like crystallites, whereas the light-colored region consists of orthogonal crystallites. EDS analysis results showed that the light-colored region is rich in WO$_3$ while the dark-colored region is rich in TeO$_2$ and B$_2$O$_3$. Considering the BEI micrographs, EDS and XRD analysis, it was found that the grain-like crystallites correspond to the $\alpha$-TeO$_2$ and B$_2$O$_3$ phases and the orthogonal crystallites belong to the WO$_3$ phase.
5. Conclusions

Developing optical fibers and amplifiers is a complex task due to the problems associated to their design and production, and due to the absence of materials having all the required properties. Tellurite glasses have recently drawn considerable attention as promising materials for optical communication systems. In order to use tellurite glasses in optical applications, a detailed microstructural characterization is crucial to obtain a desired property or behavior. This mini-review is an important informational tool for the audience to have a complete understanding on the microstructural characterization of crystallization behavior and phase separation process in different binary and ternary tellurite glass systems.

References