Nano Crystallites and Clustered Species in Modified Sodium Telluride Glasses.

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Abstract

The structural properties, crystalline and clustering behavior of $x\mathrm{Na_2O}\cdot(1\text{-}x)\mathrm{TeO_2}$ ($15 \leq x \leq 65$ mol%) glasses have been investigated by FTIR spectroscopy, X-ray diffraction (XRD), differential scanning calorimetry (DSC) and scanning electron microscopy (SEM). The experimental results have demonstrated that the basic structural units in telluride glasses change from highly strained $\mathrm{TeO_4}$ trigonal bipyramids to more regular $\mathrm{TeO_3}$ units containing non bridging oxygen atoms (NBO). The concentration of NBO atoms in telluride network increases with increasingĺ $\mathrm{Na_2O}$ content. The present results suggest that (NBO) atoms in telluride glasses exist in their pure form in compositions of up to 35 mol% $\mathrm{Na_2O}$. But at higher $\mathrm{Na_2O}$ concentrations, NBO atoms do not exist in their pure form; that is, the majority of NBO atoms are coordinated with high concentration from Na cations to form nano-crystalline clusters. The results based on X-ray diffraction (XRD), scanning electron microscopy (SEM) and differential scanning calomerty (DSC) reveal the presence of two crystalline phases: α TeO2 and $\mathrm{Na_2Te_4O_9}$ phases during the crystallization process of the prepared glass in the region < 50 mol% $\mathrm{Na_2O}$. But at higher $\mathrm{Na_2O}$ concentrations, $\mathrm{Na_2Te_2O_5}$ and $\mathrm{NaTeO_3}$ crystalline clustered phases in the nono size scale are the dominant types. This means that NBO in TeO3 trigonal pyramids will interact with the excess of Na cation resulting in the three-dimensional network containing nano size clusters particularly in telluride glasses containing 50 and 65 mol% $\mathrm{Na_2O}$. An increase in $\mathrm{Na_2O}$ concentration in $\mathrm{Na_2O}$-rich telluride network results in increasing Na coordination instead of breaking more tellurium–oxygen bonds.

Keywords

Crystalline species, Clustered phases, Spectroscopy, Glasses

1- Introduction

The structure of binary and ternary telluride glasses [1-5] has been investigated extensively by a variety of experimental techniques [5, 6]. It has been reported that the structure of TeO_2 glasses with a small amount of Na_2O (up to 20 moles %) is a continuous random network of TeO_4 trigonal bipyramids (tbps) and TeO_{3+1} polyhedra having one nonbridging oxygen, NBO. In glasses containing 20–30 % mole % Na_2O, with increasing NBOs, the TeO_3 trigonal pyramids (tps) are formed in the continuous network. At nearly 50 % mole of modifier oxide the glass structure consists of TeO_{3+1} polyhedra and TeO_3 tps along with the isolated $Te2O_5^{2-}$ and TeO_3^{2-} units. There are some types of crystalline phases appeared in glass of 50 mol% Na_2O. Which is indexed to (Na_2TeO_3) [4, 5]. Formation of such stable crystalline phases is confirmed to be related to the high concentration of NBO atoms in telluride as well as in silicate glasses [4]. In general, the structure of alkali telluride glass was tellurium atom (Te) bonded to four oxygen atoms. Some of oxygen atoms were bonded to two Te atoms (bridging oxygen, BO) and some to only one Te atom (NBO) [4, 7, and 8]. The alkali ions were arranged in random holes throughout the tellurium oxygen network. The modifier oxide such as Na_2O is consumed for the replacement of a BO with two NBOs upon addition of each Na_2O. The negative charge of the NBOs is therefore balanced by the positively charged sodium cation in order to maintain charge neutrality. This reflects that each Na atom is associated with one NBO atom. As a consequence, in pyro-telluride glasses, there are two types of oxygen, BO and NBO. But in glasses rich with higher modifier (orthotellerate composition> 50 mol %), the structural role of Na_2O is not clear and no studies on network modification in such a case is reported. Some studies [4, 9] were carried out on modified silicate and borosilicate glasses enriched with Na_2O and it was evidenced that some of crystalline clusters from the modifier such as Na can be constructed by the effect of NBO.

2- Experimental

2.1 sample preparation

Glasses of compositions $xNa_2O \cdot (100-x) TeO2$, mol%, with x=15, 25, 35, 50, 65 were prepared by melting well-mixed, high-purity raw materials of TeO_2 (99.99%) and Na_2CO_3 (99.95%) in a silica crucible at 850 °C for 1 h in air. The met was then quenched between two stainless steel plates. .The as obtained glasses were immediately stored in a vacuum desiccator until used for measurements.

2.2 Experimental Techniques and Measurements

X-ray diffraction measurements were carried out on powdered samples using a Bruker D8 Advance powder XRD system with a Cu K・・radiation. The range of the diffraction angle (2・・ is changed from from 5° to 80° using a dwell time of 0.4 seconds. The X-ray diffraction is used to confirm the amorphous or crystalline nature of the material structure.

FTIR Spectra were obtained in the wavenumber range of 400 to 4000 cm^{-1} using a Mattson 5000 FTIR Spectrometer. Each sample was mixed with KBr by the ratio 1:100 in weight and then pressed to produce a homogeneous pellet. The infrared absorbance measurements are measured at room temperature and immediately after preparing the pellets.

Scanning electron microscopy is widely used to examine surface modifications and microstructure of specimens using (JEOL SEM Model, JSM-5610 Lv). In this measurement, a beam of electrons is focused on a spot volume of the specimen, resulting interaction of the beams with the surface of the sample. The scattered electrons can be detected and provide information on surface morphology.

The energy dispersive X-ray spectra (EDX) of the samples were also acquired during their scanning electron microscopic (SEM) measurement. EDX is based on the detection of the emitting of x-rays by the elements of the sample as a result of the ejected inner shell electrons using a high energy electron beam. The EDX spectrum normally displays peaks corresponding to how frequently an X-ray is received for each energy level in the single element. The higher concentrated elements in the sample present the most intense peaks in the spectrum. This technique is widely used for identifying the elemental composition of the sample.

3. Results and Discussion

It was reported recently [4,9,10] that alkali lead silicate or borosilicate glasses containing extremely high concentration from modifier oxide and NBO can simply form cluster species from the modifier captions around the NBO. The well formed clusters can be distributed in a specific manner which allows to some percolation channels or pathways to be formed in the main glass network. The micro-segregations of the modifier oxide (Na_2O) is dominant in glasses enriched with modifier oxide, i.e., of concentration greater than 30 mol%. But at lower concentration, Na_2O is consumed as an ordinary modifier creating NBO atom in the main glass network without any tendency toward building any types of ordered clustered species.

The above consideration is supported to a great extent by the present experimental studies of Na_2O rich telluride glasses, since the obtained results have showed that Na can play a role of a clustering agent when the concentration of Na_2O is relatively high (≥ 35 mol%). As a result of presence of high contents of modifier oxide, telluride polyhedral units such as isolated $Te2O_5^{2-}$ and TeO_3^{2-} groups with NBO atoms are formed. Such units can activate both crystallization and clustering process in the main glass network [4, 9].

3.1 DSC Thermal analysis

The DSC curves of the investigated glasses in this study are shown in figures 1and 2. As presented by figure 1(a), the DSC curve for the glass containing 15 % mole% of Na_2O shows sharp crystallization peak at 320^oC indicating crystallization of a single crystalline phase of the type $Na_2Te_4O_9$ [1,11,12]. But glass with 35 % mole % Na2O contains a broad asymmetric exothermic peak at ≈ 345^oC, figure 1(b). This broad shape of the crystallization peak may be attributed to simultaneous crystallization of more than one phase. It is well known, that sharp crystallization peak implies a higher order reaction due to bulk crystallization of three dimensional growths. While a broad peak signifies a lower order due to surface crystallization of one dimensional growth [13].

Glasses of higher Na_2O concentrations (50 and 65 mol %) showed different crystallization peaks figure 2(a, b). These exothermic peaks corresponding to the aggregation of different crystalline cluster species [13, 14]. As a result of crystallization process , the one specific phase in the parent glass (15 mol% Na2O) is transformed into new crystalline phases represented by the appearance of more additional exothermic peaks in glasses enriched with Na_2O (50 and 60 mol%) see figure 2 (alb). Such ego thermal peaks are typical for glasses with high crystallization tendency and also give preliminary guidance for the structure changes to obtain clustered glasses or glass ceramics [14]
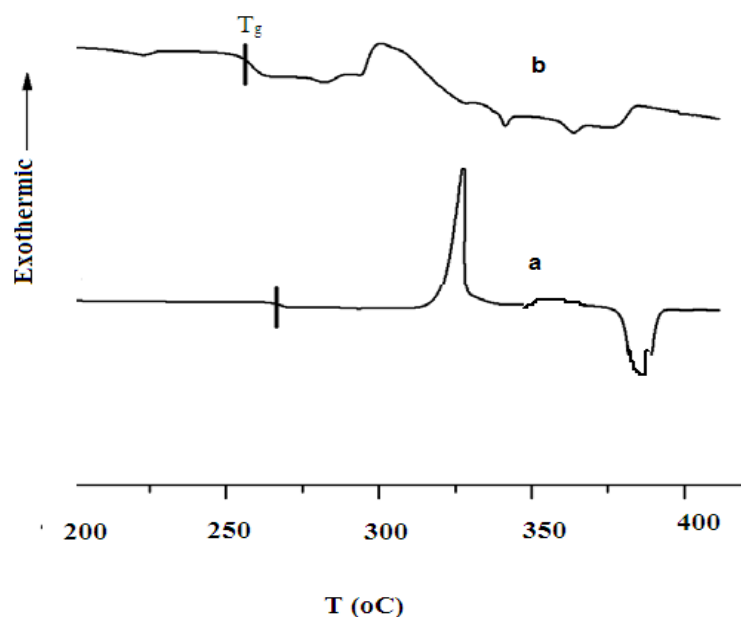

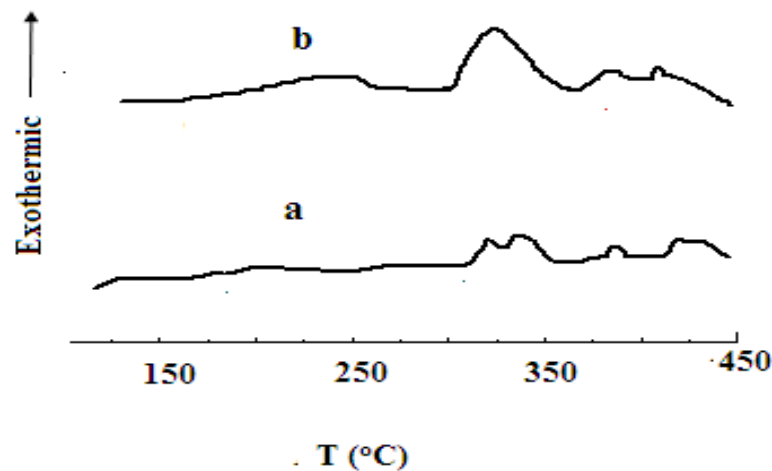Figure 1 Differential scanning calometry for glasses containing Na_2O. A (20 mol %.), b (35mol %)

Figure 2 Differential scanning calometry for glasses containing Na_2O. A (50 mol %.), b (65mol %)

It can be also noticed that the position of exothermal peak shifts toward higher temperature with increasing Na_2O concentration. In addition, more exothermic peaks are found in glasses containing higher Na_2O concentrations (50, 65 mol %) (Figure 2) in comparison with glasses of lower Na_2O concentration (figure 1). These differences may be attributed to formation of different types of nano-size clusters or crystallites of Na2Te4O9 and Na_2TeO_3 species whose concentration increases with increasing the Na_2O content [1, 12-14].

3.2 XRD Analysis

Figure 3 shows changes of XRD spectra with change of glass composition. The spectrum for the as prepared pure vitreous TeO_2 is also shown (figure 4) for comparison. The spectrum of pure TeO_2 glass (figure 4) is dominated by several diffraction peaks which may be assigned to ordered TeO_2 network made of chain – like fragments, consisting of the rather symmetric Te-O-Te bridges and Te-O terminal bonds [1-7]. The more ordered structure is disrupted to great extend by adding Na_2O in the region (20-35 mol %), figure 3(a, b) and then recrystallization is appeared again at higher Na_2O concentration. More crystalline structure is considered in Na_2O rich glasses, see figure 3(c, d).

The interpretations based on the data of DSC techniques are highly confirmed by XRD results based on X-Ray spectroscopy of the same glasses. It can be concluded from figure 3(a) that the amorphous structure is confirmed in glasses of up to 30 mol% Na_2O. On the other hand, crystalline structure is evidenced upon more Na_2O addition, since it can be seen from figure 3 that XRD spectra of glasses of relatively high content of modifier oxide contain several components of sharp diffraction lines. This means that the crystallinity is enhanced via increasing Na_2O content which is considered due to increase the aggregation of Na around NBO atoms [4]. According to JCPDS data, the small diffraction peaks in the XRD pattern of glass containing 15 and 25 mol% Na_2O correspond to those for a-TeO_2 (PDF 42-1365), whereas for crystallized glass containing more higher Na_2O content (35- 65 mol%) involves diffraction pattern of additional peaks which are indexed and related to $Na_2Te_4O_9$ (PDF 32-1166), $Na_2Te_2O_5$ and Na_2TeO_3[15]. Presence of such crystalline phases is expected since these glasses are enriched with modifiers and NBO atoms which activate the aggregation of Na cation around NBO atoms forming aggregated crystalline species enriched with sodium [4].

However, the little diffraction peaks for lower values of Na_2O (20 mol %) do not match with the peaks for $Na_2Te_2O_5$ but the peak at about 12° may be related to Na2TeO4 available in the JCPDS files.
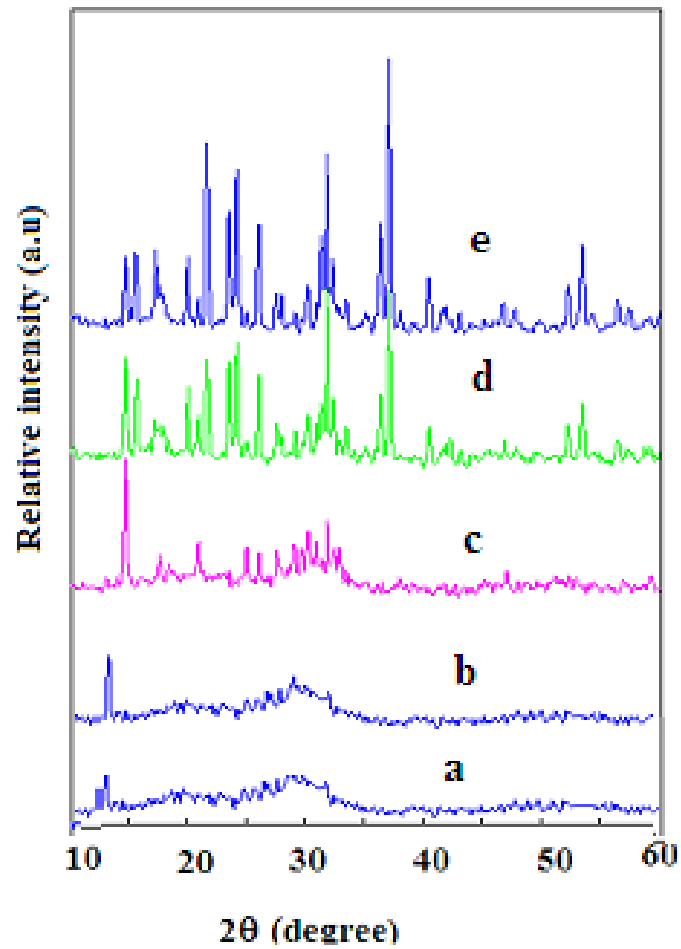
Figure 3 XRD patterns for glasses containing Na_2O. a (20 mol%.), b (25 mol%), C(35 mol%) and d (50 mol%) and e (65 mol%).
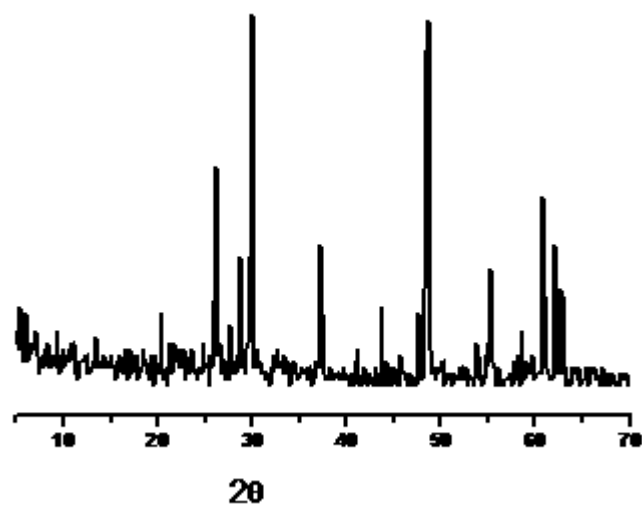

Figure 4 XRD pattern of pure TeO_2 glass

3.3 FTIR spectroscopy

Figure 5 shows the infrared absorption spectra for the sodium telluride glass samples in the 400 - 4000 cm^{-1} range. The spectrum for prepared pure vitreous TeO_2 is also shown for comparison. The spectrum of TeO_2 glass (plot an in figure 5) is dominated by two absorption bands at 775 and 660 cm^{-1}. The band at 775 cm^{-1} is assigned to the symmetric equatorial $(TeO_2)_{eq}$ vibration, while the broad non-symmetric band at 660 cm^{-1} may represent symmetric and asymmetric axial $(TeO_2)_{ax}$ stretching modes of TeO_4 units [4,6,11,12]. It was suggested that, the TeO_2 glass is made of chain – like fragments, consisting of the rather symmetric Te-O-Te bridges (responsible for the band near 775 cm^{-1}), and of the Te-O terminal bonds. The latter type of bonds interconnects the neighboring chains via very asymmetric Te-$O_{terminal}$ -Te. The bending vibrations of those bonds account for the band near 660 cm^{-1} [1-6].

FTIR absorbance spectra (figure 6. plot b, c, d and e) show that the addition of Na_2O to TeO_2 glass affects the obtained spectra. Generally, the feature of FTIR spectra is changed upon increasing Na_2O concentration as is seen from figure 6. The observed trend is that as Na_2O content increases at expense of TeO_2, the high frequency absorption peak (1500 cm^{-1}) showed a gradual increase. Moreover, the spectrum line-shape changes clearly when Na_2O content varies between 0- 65 molpercent. The most to be noted is that the absorbance   band found around 1500 cm^{-1} becomes more resolved in glasses of high Na_2O contents (50 and 65 mo%). Quantitively, the relative area of this band increases with increasing Na_2O content as represented in (Figure 7). Same behavior was found in silicate glasses rich with Na_2O [4-6]. In such situation, there are two phases are formed upon increasing Na_2O contents. Na-rich regions and tellurium rich phase. These tow distributions can be extended in three dimension to form sodium and NBO rich channels within tellurium rich regions. It is consequently considered that an inhomogeneous distribution of structural groups would be formed in the glass matrix. The non-bridging oxygen atoms can simply provide specific structural links between two sub-structural units, with the result that Na atoms cluster around the NBO resulting in the formation of percolation channels. The micro-segregations of Na_2O from SiO_2 or TeO_2 are more significant for sodium concentration greater than 30 mol%. As is seen from FTIR spectra, the resolving of absorbance band around 1500 cm^{-1} in glasses of 50 and 65 mol% Na_2O confirms the formation of crystallized aggregated clusters from Na_2O. This consideration is supported to great extent by the present experimental studies of Na rich telluride glasses, since the obtained results show that Na is clustering and consequently the extended glass network is heterogeneous when the concentration of Na_2O is high ($\geq$ 50 mol%).
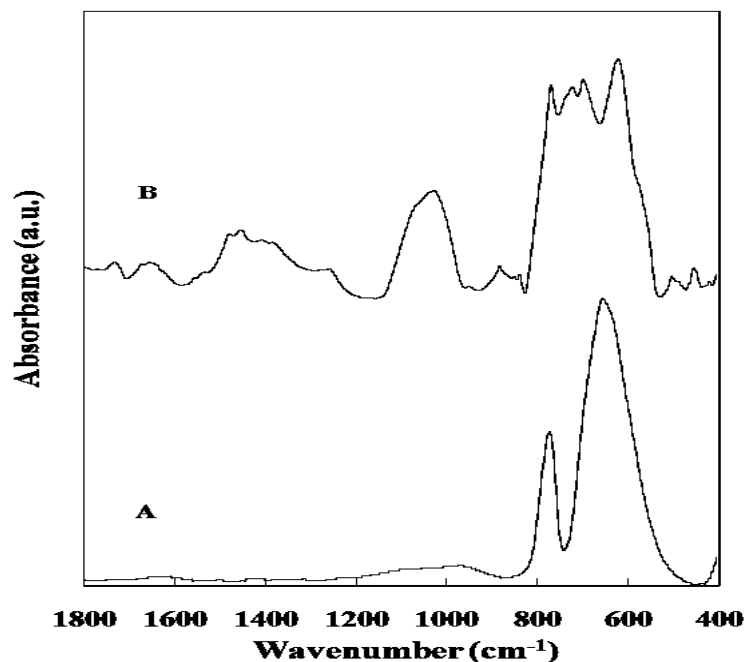
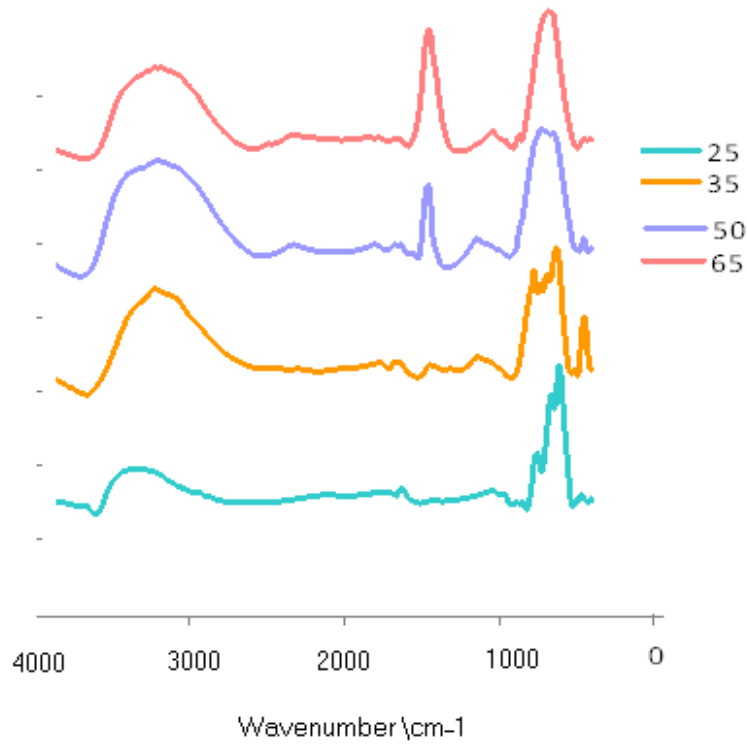Figure 5 the infrared absorption spectra for pure TeO2 (A) and of the sodium telluride glass sample (B) in the 400 - 4000 cm^{-1} range

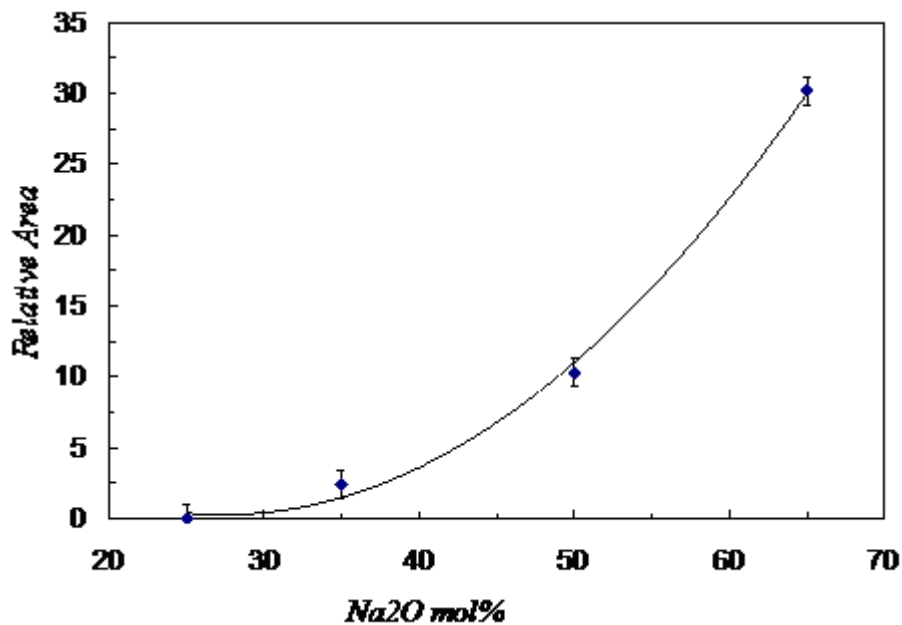Figure 6   FTIR spectra for glasses containing different Na$_2$O concentrations

Figutr 7 Change of relative area of FTIR peak at 1500 cm^{-1} with Na$_2$O concentration

Moreover, appearance of new peak at about 1400 cm^{-1} in glasses rich with Na$_2$O (≥ 50 mol%) and the peaks around 505-455 cm^{-1} indicate the formation or precipitation of fused Na$_2$O clusters   [4-6]. The increasing of cluster concentration results in increasing relative area of the peaks centered around 1400 cm^{-1}.

Moreover the splitting of the absorption bands at 455, 505, 1048 and 1097 cm^{-1}[4-8] is transformed to one resolved peak which may be assigned to segregation and separation of Na$_2$O phases deposited on amorphous TeO$_2$ network This band shifts to a position between 1456 and 1481 cm^{-1} which is due to distribution of different Na sites that depend on nucleation, segregation and formation of Na$_2$O cluster [4-6].

It is therefore deduced that formation of a new resolved band at 1400 cm^{-1} especially at high Na$_2$O concentration and transformation of the splitted peaks (600-800cm^{-1}) to one resolved absorption spectrum may be related to formation of separated clusters [4-6], which was documented by SEM morphology and XRD results

The development of the first sharp absorption peak of sodium tellurate glasses at 1400 cm^{-1} which increase with increasing Na$_2$O contents was interpreted on basis of heterogeneous Na distribution in the network of the glass.

3.4 SEM-EDS Investigation

SEM-EDS investigations were performed on some selected glass compositions in order to identify changes in morphology and chemical composition of the investigated samples. Three selected samples, one of low Na$_2$O content (20 mol %) and the other samples contain the highest Na$_2$O concentration (50 and 65 mol %) have been chosen.

The SEM micrograph in Figure 8 for the glasses containing 20 mole Na2O showing homogeneous glassy phase which is typical for the low Na$_2$O composition. The corresponding EDS analysis showed identical spectra confirming homogeneous character of the sample. This result is further supported from XRD pattern of the glass of the same composition (20 mol% Na$_2$O), since no crystals were detected by XRD spectroscopy. The chemical composition calculated from EDS spectra of glass of 20 mol% Na$_2$O (19.5 % mole of Na$_2$O and 79 ± 0.5 % mole% of TeO$_2$) is in excellent agreement with nominal composition of the glass.

Figure 9 shows the SEM micrograph taken from the surface of the crystallized glass containing 50 and 65 % mole % of Na$_2$O. The morphology of the samples consists of hexagonal-shaped crystals with diameter ranging from 5 to 10 mm. Based on the EDS analysis, observed crystals are Cleary observed indicating crystallization of phase with Na$_2$Te$_2$O$_5$ stoichiomery which is fitted and matched with the pattern for Na$_2$Te2O5 available in JCPDS files, so it seems that the observed crystals correspond to a new Na$_2$Te$_2$O$_5$ polymorph.
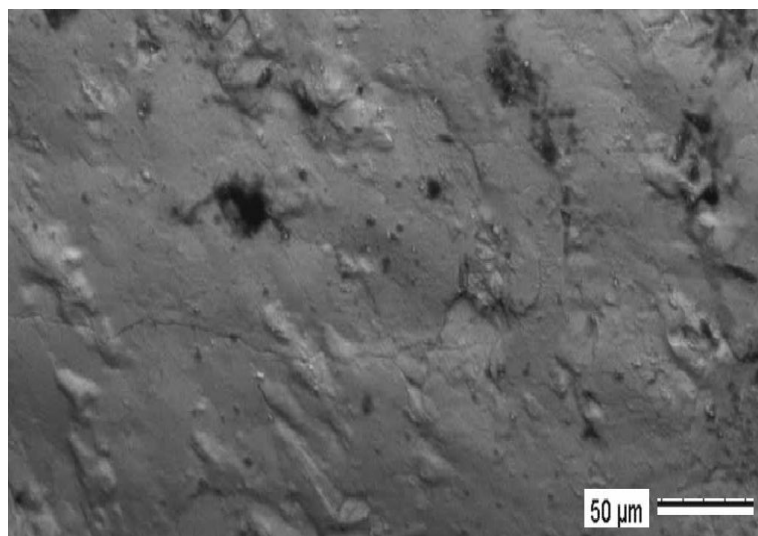
(20 mol %)
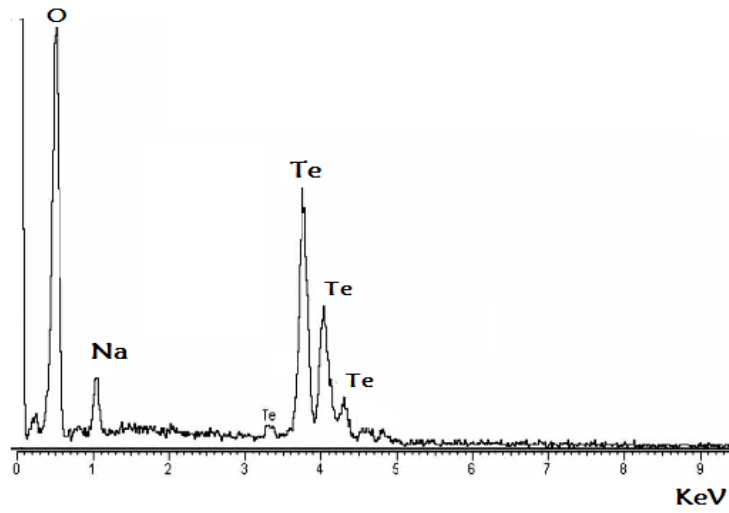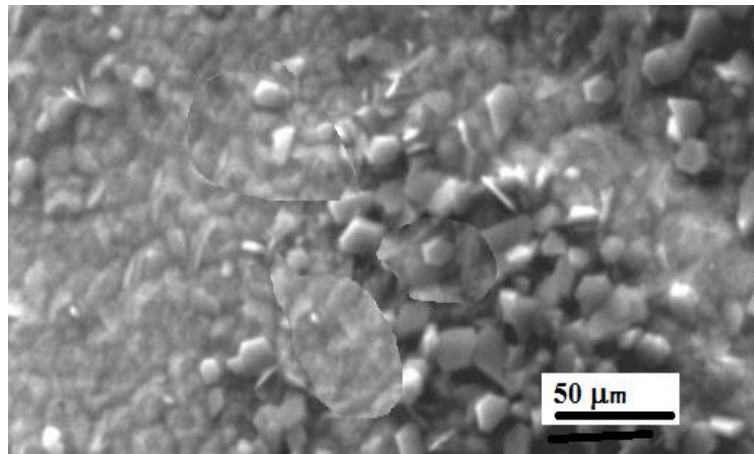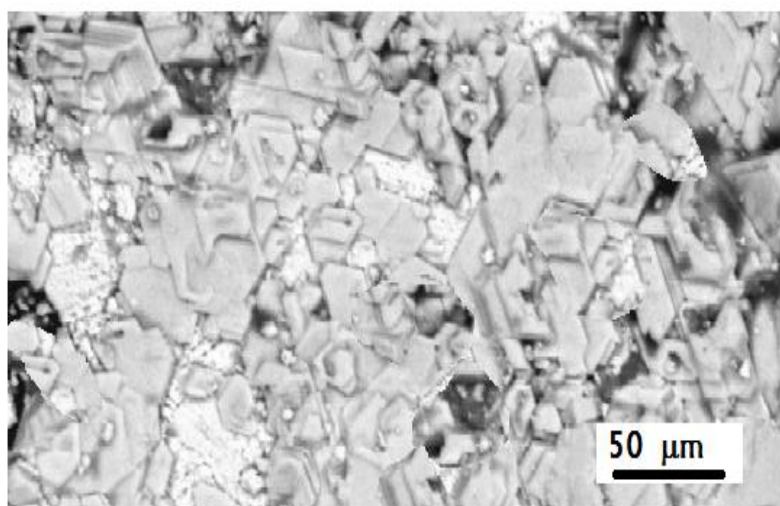
Figure 8 SEM and ED's spectra for glass containing 20 mol% Na$_2$O
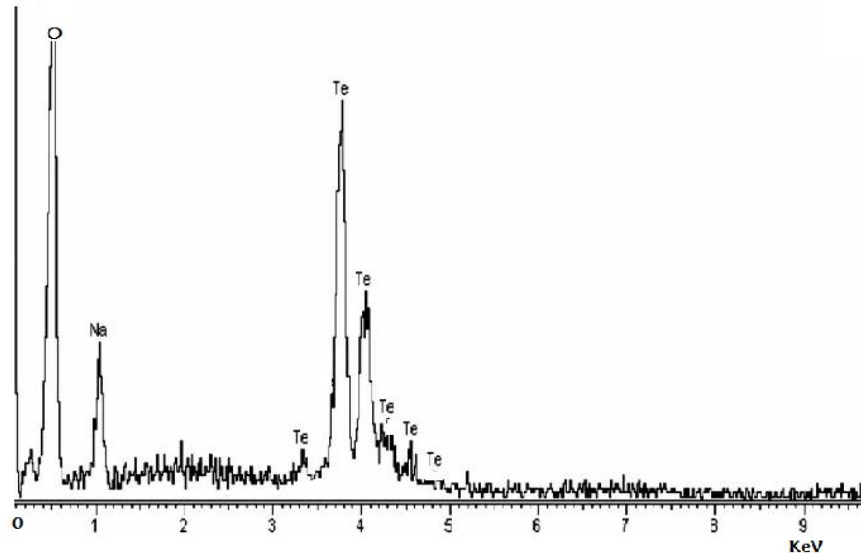

(50 mol %)

(65 mol %)

Figure9 SEM and EDS spectra for glass containing 50 and 60 mol% Na$_2$O

4- Conclusion

The obtained results have demonstrated that the basic structural units in telluride glasses change from highly strained TeO$_4$ trigonal bipyramids to more regular TeO$_3$ units containing non bridging oxygen atoms (NBO). The concentration of NBO atoms increases with increasingĺ Na$_2$O content. (NBO) atoms in telluride glasses exist in their pure form in glasses of up to 35 mol% Na$_2$O. But at higher Na$_2$O concentrations, NBO atoms do not exist in their pure form; that is, the majority of NBO atoms are coordinated with high concentration from Na cation to form nano-crystalline clusters. X-ray diffraction (XRD), scanning electron microscopy (SEM) and differential scanning calomerty (DSC) reveal the presence of two crystalline phases: α TeO$_2$ and Na$_2$Te$_4$O$_9$ during in the region < 50 mol% Na$_2$O. But at higher Na$_2$O concentrations, Na$_2$Te$_2$O$_5$ and NaTeO$_3$ crystalline clustered phases in the nono size scale are the dominant types... In Na$_2$O-rich telluride network, Na coordination is the dominant process instead of breaking more tellurium–oxygen bonds.

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