SYNTHESIS OF ZnTeO₃ BY CRYSTALLIZATION OF GLASSES IN TeO₂-Bi₂O₃-ZnO-Nb₂O₅ SYSTEM

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In memory of Prof. D.Sc. Yanko Dimitriev

ABSTRACT

The aim of the present work is to verify the synthesis of zinc tellurite by crystallization of glasses in TeO₂ - Bi₂O₃ - ZnO - Nb₂O₅ system. The investigation refers to TeO₂-based glasses containing up to 10 mol % of Nb₂O₅ and Bi₂O₃ and ZnO content ranging from 5 mol % to 10 mol %. Several glasses are selected and heat treated for 6h at 500°C. The XRD analysis detects formation of several ZnTeO₃, TeO₂ and ZnO crystalline phases. Additional information for the formation of ZnTeO₃ crystalline phase is obtained by infrared spectroscopy (IR). There is a difference in the IR spectra of the crystalline sample of 50TeO₂.50ZnO (ZnTeO₃) and those of the multicomponent glasses. The spectra analysis shows that the glass network consists mainly of TeO₄ (tbp) units, while TeO₅ (tp) are the main structural units in the crystalline ZnTeO₃ phase. The microstructure of the selected crystallized samples is examined by SEM analysis.

Keywords: tellurite glasses, crystallization, phase transformations, structure.

INTRODUCTION

Tellurite glasses and glass ceramics are promising materials due to their high refractive index (larger than 2), wideband infrared transmittance (extending up to 6 micrometer), and large third-order nonlinear optical susceptibility [1]. That is why over the past twenty years, tellurite glasses have been of an increasing scientific interest. It is well known that these glasses are also a subject of intensive investigations because they can form a glassy phase over a wide concentration range [1]. Tellurium(IV) oxide in combination with ZnO forms stable glasses [2]. Binary ZnO-TeO₂ system is a basic one that has good glass-forming ability (9 mol % - 40 mol % of ZnO) and has been studied by many researchers [1]. Multicomponent optical glasses are obtained [1] on its basis. The glass forming tendency as well as the different structural and optical properties of ZnO-TeO₂ system are well investigated [2, 3] with the application of IR, Raman, EXAFS.

Two compounds are known to exist in ZnO-TeO₂ system: Zn₅Te₆O₁₆ and ZnTeO₃ [2]. They are structurally investigated in details [4, 5]. These compounds are a subject of increased scientific interest due to their interesting properties. Recently, data concerning the synthesis and optical properties of ZnTeO₃ and Zn₂Te₃O₈ under varied experimental conditions has been reported [6]. The optical and electrical properties of ZnTeO₃ single crystals are reported by Nawash et al. [7].

Generally, it is necessary to control the process of
crystallization during the synthesis of zinc-tellurite glass compositions. Many authors have made an attempt to understand how to suppress the crystallization during the fabrication of glasses in different systems containing ZnO and TeO$_2$ [8 - 11]. To best of our knowledge, this topic has not yet been exhausted.

Dimitriev et al. [12 - 15] have investigated for many years the formation and the structure of non-traditional tellurite glasses. A lot of fundamental results concerning the type of the structural units building up the amorphous network have been obtained and they are reported in a series of papers. Generally, it is established that the short range order of tellurite glasses consists of TeO$_3$, TeO$_4$ or combinations of these polyhedra [12 - 15].

The present paper is a continuation of our previous investigations on the multicomponent TeO$_2$ – Bi$_2$O$_3$ – Nb$_2$O$_5$ – ZnO system, where the influence of TiO$_2$ on the thermal stability and crystallization of selected glasses is studied [11]. The aim of the present work is to verify the synthesis of ZnTeO$_3$ by crystallization of glasses in the multicomponent TeO$_2$ – Bi$_2$O$_3$ – Nb$_2$O$_5$ – ZnO system.

**EXPERIMENTAL**

**Preparation of glasses**

All samples subjected to detailed investigations are shown in Table 1. The batches were prepared using reagent grade TeO$_2$, Bi$_2$O$_3$, Nb$_2$O$_5$ and ZnO. 10 grams of each were homogenized and were melted in air for 15 min - 20 min using alumina crucibles at temperatures between 900°C-1000°C. The melting temperature was selected depending on the composition. The glass forming ability of the compositions was determined by pouring of the melts between two copper plates at a cooling rate of 10 K/s - 10$^2$ K/s. The obtained glasses were transparent and bright yellow coloured. Several compositions, situated in different part of the system were selected: 72TeO$_2$.10ZnO.9Bi$_2$O$_3$.9Nb$_2$O$_5$ (VI-glass), 64TeO$_2$.20ZnO.8Bi$_2$O$_3$.8Nb$_2$O$_5$ (6A-glass), 56TeO$_2$.30ZnO.70Bi$_2$O$_3$.7Nb$_2$O$_5$ (6B-glass), 32TeO$_2$.60ZnO.4Bi$_2$O$_3$.4Nb$_2$O$_5$ (6H-glass and crystals) and 48TeO$_2$.40ZnO.6Bi$_2$O$_3$.6Nb$_2$O$_5$ (6F-glass). The binary composition 50TeO$_2$.50ZnO (TZ), containing pure ZnTeO$_3$ was used for a comparison. All compositions were subjected to an additional heat treatment for 6h at 500°C.

**Samples characterization**

The phase formation of the powdered samples was established by X-ray phase analysis with a Bruker D8 Advance diffractometer using Cu Kα radiation in the 10 < 2θ < 80 range. The differential thermal analysis (DTA) of selected compositions was carried out on STA PT1600 with Pt/Pt/Rh thermocouples with a heating rate of 10 K/s in an air flow, using Al$_2$O$_3$ as a reference material. The morphology of the samples was examined by scanning electron microscopy (SEM) using a JEOL JSM 6390 electron microscope (Japan) equipped with ultrahigh resolution scanning system (ASID-3D). The IR spectra of the glasses were recorded in the 1400 cm$^{-1}$ - 400 cm$^{-1}$ region using KBr pellet technique (Nicolet-320 FTIR spectrometer).

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**Table 1. Investigated compositions in the TeO$_2$-ZnO-Bi$_2$O$_3$-Nb$_2$O$_5$ system.**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Compositions</th>
<th>XRD data</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>50TeO$_2$.50ZnO</td>
<td>ZnTeO$_3$</td>
</tr>
<tr>
<td>TZ</td>
<td>72TeO$_2$.10ZnO.9Bi$_2$O$_3$.9Nb$_2$O$_5$</td>
<td>glass</td>
</tr>
<tr>
<td>VI</td>
<td>64TeO$_2$.20ZnO.8Bi$_2$O$_3$.8Nb$_2$O$_5$</td>
<td>glass</td>
</tr>
<tr>
<td>6A</td>
<td>56TeO$_2$.30ZnO.70Bi$_2$O$_3$.7Nb$_2$O$_5$</td>
<td>glass</td>
</tr>
<tr>
<td>6B</td>
<td>48TeO$_2$.40ZnO.6Bi$_2$O$_3$.6Nb$_2$O$_5$</td>
<td>glass</td>
</tr>
<tr>
<td>6F</td>
<td>32TeO$_2$.60ZnO.4Bi$_2$O$_3$.4Nb$_2$O$_5$</td>
<td>glass + cryst.</td>
</tr>
<tr>
<td>6H</td>
<td>48TeO$_2$.40ZnO.6Bi$_2$O$_3$.6Nb$_2$O$_5$</td>
<td>glass + cryst.</td>
</tr>
</tbody>
</table>
RESULTS AND DISCUSSION

Phase transformations

Transparent and pale yellow glasses containing more than 40 mol % of TeO$_2$ (Table 1) are obtained. The X-ray diffraction patterns of selected glass samples (VI, 6A and 6F) are shown in Fig. 1(a), while that of the glass - crystalline one (6H) is presented in Fig. 1(b). The latter figure shows that ZnO (JCPDS 36-1451) and ZnTeO$_3$ are detected upon free cooling of the melt. The XRD pattern of the binary sample 50TeO$_2$.50ZnO where crystalline ZnTeO$_3$ (JCPDS 44-0240) phase are detected is shown in Fig. 1(c).

The thermal parameters of selected quenched glass samples (VI and 6F) are obtained from DTA curves (Fig. 2). They are characterized by a glass transition temperature ($T_g$) at 330°C and 370°C and glass crystallization temperature ($T_x$) above 400°C. It is obvious that the glass of a higher TeO$_2$ content (72 mol %, sample VI) exhibits a lower value of the glass transition temperature (330°C). The additional heat treatment of the samples (500°C for 6h) is carried out in view of DTA results obtained (Fig. 2), our previous investigations [11, 15, 16], as well as some literature data [17, 18]. The main crystalline phases that are detected after crystallization refer to TeO$_2$ (JCPDS 52-0795), ZnO (JCPDS 36-1451), ZnTeO$_3$ and two bismuthate crystalline phases: Bi$_2$Te$_4$O$_{11}$ (JCPDS 01-081-1330) and Bi$_2$Te$_2$O$_7$ (JCPDS 52-1260) (Fig. 3). As seen from the figure TeO$_2$ is separated only in the sample of the highest TeO$_2$ content, while a mixture of simultaneously existing crystalline phases is detected in the other samples (of TeO$_2$ content ranging between 40 mol % - 64 mol %). The other peculiarity is that crystalline ZnTeO$_3$ phase is predominantly separated only in samples containing more than 20 mol % of ZnO and below 9 mol % of Bi$_2$O$_3$. Obviously, the presence
of a higher Bi₂O₃ content (above 10 mol %) suppresses the ZnTeO₃ formation and bismuth containing phases crystallization upon additional heat treatment (Fig. 3).

SEM observations

SEM observations of selected samples 50TeO₂-50ZnO (TZ), 32TeO₂.60ZnO.4Bi₂O₃.4Nb₂O₅ (6H) and 48TeO₂.40ZnO.6Bi₂O₃.6Nb₂O₅ (6F-glass), heat treated for 6h at 500°C are performed (Fig. 4(a, b)). Partial crystallization is observed, but most of the sample volume is still amorphous. The preliminary microprobe chemical composition analysis shows the presence of ZnTeO₃ phase that is in agreement with XRD results (Fig. 3).

IR structural investigations

The IR spectra of the investigated samples are shown in Fig. 5 (a, b). Fig. 5(a) shows the IR spectra of multi-component glass compositions, while Fig. 5(b) presents the IR spectrum of a binary crystalline sample (TZ). The assignment of the bands is made in the framework of the local point symmetry approaches following the methods developed by Nakamoto and Tart [19, 20]. Two well resolved bands of maxima near 630 cm⁻¹ - 620 cm⁻¹ and 480 cm⁻¹ - 470 cm⁻¹, as well as shoulders near 870 cm⁻¹ and 780 cm⁻¹ - 770 cm⁻¹ are observed in the IR spectra of all glasses. According to the literature data [12-14] as well as our previous studies on tellurite glasses [21, 22], the intensive band at 635 cm⁻¹ (νₛ) with a shoulder at 675 cm⁻¹ (νₐₛ) are characteristic for TeO₄ (tbp) units. The weak band at 780 cm⁻¹ is ascribed to the symmetric stretching vibrations (νₛ) of TeO₄ units [21, 22]. In view of the obtained results it can be assumed that the structure of investigated glasses (short range order) is determined mainly by TeO₄ units (bands at 770 cm⁻¹, 630 cm⁻¹ - 620 cm⁻¹). They most probably participate in the formation of bridging Te–O–Te bonds. Nevertheless, the intensive band at ca 470 cm⁻¹, which obviously is a complex one, is due probably to the vibrations of dif-

![Fig. 3. XRD patterns of samples heat treated at 500°C for 6h.](image)
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Different building units such as BiO₄ and ZnO₄ [23]. The symmetric vibrations of Te–O–Te bridges connecting different tellurite complexes are also in this spectral region. All spectra show a weak band at ca 870 cm⁻¹. The bands around 957 cm⁻¹ - 880 cm⁻¹ could be attributed to the stretching vibrations of NbO₆ building units according to Y. B. Saddeek et al. [24] who study the structural peculiarities of TeO₂/Nb₂O₅ glasses.

CONCLUSIONS

Glasses were prepared in the multicomponent TeO₂ – ZnO – Nb₂O₅ – Bi₂O₃ system with the application of the melt quenching method. They exhibited good thermal stability up to 400°C. It was proved that the short range order of the amorphous network was determined mainly by TeO₄ structural units. The heat treatment (6h at 500°C ) led to obtaining polycrystalline samples whose content referred mainly to TeO₂, ZnTeO₃ and ZnO. The crystalline ZnTeO₃ phase was separated predominantly in compositions containing more than 50 mol % of TeO₂, more than 20 mol % of ZnO and less than 9 mol % of Bi₂O₃.

REFERENCES

2. V. Kozhukharov, H. Bürger, S. Neov, B. Sidzhimov, Atomic arrangement of a zinc-tellurate glass,