Influence of modifiers on thermal and optical properties of TeO$_2$–P$_2$O$_5$–ZnO–PbF$_2$ glasses

MANUELA REBEN$^1$, BOŻENA BURTAN-GWIZDAŁA$^2$, JAN CISOWSKI, IWONA GRELOWSKA$^1$, EL SAYED YOUSEF$^{3, 4}$, JULITA BUKALSKA$^5$

$^1$Faculty of Materials Science and Ceramics, AGH – University of Science and Technology, al. Mickiewicza 30, 30-059 Cracow, Poland

$^2$Institute of Physics, Cracow University of Technology, ul. Podchorazych 1, 30-084 Cracow, Poland

$^3$Department of Physics, Faculty of Sciences, King Khalid University, P.O. Box 9004, Abha, Saudi Arabia

$^4$Research Center for Advanced Materials Science (RCAMS), King Khalid University, Abha 61413, P. O. Box 9004, Saudi Arabia

$^5$Kratki.pl, W. Gombrowicza 4, 26-660 Wsola/Jedlińsk, Poland

*Corresponding author: manuelar@agh.edu.pl

A series of fluorotellurite glasses based on 70TeO$_2$–5M$_x$O$_y$–10P$_2$O$_5$–10ZnO–5PbF$_2$ in mol%, where M$_x$O$_y$ = (WO$_3$, Nb$_2$O$_5$) doped with 2400 ppm of Er$_2$O$_3$ have been prepared by the conventional melt quenching method. The influence of modifiers on thermal and optical properties of glasses has been analyzed. Thermal characteristics of glasses like the glass transition temperature $T_g$, the temperature for the crystallization onset $T_x$, the maximum crystallization temperature $T_c$, and the thermal stability parameter were determined by the DSC method. The ellipsometric data have provided Sellmeier-type dispersion relations of the refractive index of the investigated glasses. The optical parameters are used to calculate the molar refractivity, molar polarizability, oxide ion polarizability, molar cation polarizability, and a number of polarizable atoms per unit volume for every glass composition in order to interpret the refractive index of these glasses.

Keywords: fluorotellurite, thermal stability, refractive index, luminescence, Judd–Ofelt theory.

1. Introduction

Due to a significant increment in the Er$^{3+}$-doped materials, the present paper aims to report newly developed fluorotellurite glasses doped with Er$_2$O$_3$ and to examine the effect of modifiers on the thermal and selected optical properties of the obtained glasses. Fluorotellurite glasses possess some advantages of both fluoride and tellurite
glasses, such as lower phonon energy, longer red-cutting edge, and excellent chemical stability as compared to other types of glasses [1, 2]. One can say that among all oxide glasses, the tellurite glasses have the poorest thermal stability due to their low value of glass transition temperature and therefore this kind of glasses is not suitable for use in mid-infrared photonics. On the other hand, their high rare earth solubility and high transparency in a wide wavelength range make the tellurite glasses very attractive from the point of view of possible applications [3–5].

However, one of the main drawbacks of tellurite glasses is the presence of hydroxyl (OH–) groups that quenches radiative emission of rare earth (RE) ions [6]. Thus by addition of fluorine to the tellurite glass matrix it seems to be possible to reduce the OH– concentration and the electron–phonon coupling.

In last years, extensive studies have been made to fabricate tellurite glass with low OH– concentration. Most of this research is focused on the dehydration by incorporating fluoride raw materials [7–10].

There are many fluorides which were incorporated into the tellurite glass matrix, e.g., ZnF2, NaF and BaF2 [1, 11–13]. An interesting characteristic of the fluorotellurite glasses is the appearance of variations in their structural, thermal and optical properties when different modifier oxides (MgO, WO3, CaO, BaO, SrO, CdO, and PbO) are introduced. In addition, TeO2 together with other heavy metal oxides like Bi2O3, Sb2O3 or Nb2O5 produces glasses with some enhanced properties [14]. The more so, when Nb2O5 and ZnO are introduced into the tellurite glass network, thermal stability, chemical resistance and nonlinear optical performances are highly improved. Therefore, the vitreous system with composition containing TeO2 together with Nb2O5 and ZnO has received great attention owing to the possibility of its use for several practical applications [15]. This paper examines the effect of selected matrix modifiers on thermal and optical properties of a new fluorotellurite glass prepared using the melt quenching method.

2. Experiment

In this work, the glasses from the system: 70TeO2–5MxOy–10P2O5–10ZnO–5PbF2 in mol%, where MxOy = (WO3, Nb2O5) are presented. The glasses have been doped with erbium ions. In order to introduce the Er3+ ions into the glass matrix, the respective oxides of an amount of 2400 ppm of Er2O3 have been added to the batches.

The following raw materials were used to prepare the batches: tellurium oxide (TeO2), fluorite lead (PbF2), zinc oxide (ZnO), tungsten trioxide (WO3), niobium oxide (Nb2O5) and erbium oxide (Er2O3). Before melting, raw materials were pre-heated at 200, 300 and then 400°C, to eliminate or minimize the water content already present in the raw materials. The batches were put in a covered gold crucible and heated in a melting furnace to a temperature of 850°C for 30 min; the melt was stirred from time to time. The melt was poured out onto a graphite mold. Subsequently, the sample was transferred to an an-
nealing furnace and kept for 2 h at 320°C, i.e. 15°C below the glass transition temperature $T_g$. Then the furnace was switched off and the glass sample was allowed to cool. The compositions of the investigated glasses are listed in Table 1.

The thermal stability of glasses obtained against crystallization was characterized in terms of the temperature interval $\Delta T_c = T_c - T_g$, where $T_c$ is the onset of first exothermal crystallization event. The glass forming tendency parameter (Hruby parameter) $K_H = (T_c - T_g)/(T_m - T_c)$, with $T_m$, the melting temperature, was calculated. The characteristic temperatures of glass were determined by DSC measurements conducted on the NETZSCH 5 System operating in the heat flux DSC mode at a heating rate of 10°C/min. The density of glasses was measured according to the Archimedes principle using water as an immersion liquid. Concentration of Er$^{3+}$ ions in the studied glass was calculated on the basis of density measurements.

For optical measurements, the annealed glass samples were sliced and polished to dimensions of about 10 × 10 × 2 mm$^3$. The ellipsometric data were collected with a M-2000 Woollam ellipsometer in the spectral range 190–1700 nm. Knowledge of $\Psi$ and $\Delta$ allows one to determine not only the dispersion of the optical constants, but also the roughness $\sigma$ of a glass [16]. The samples have been measured for three angles of incidence, namely 60°, 65° and 70°. To analyze the data, we have combined all the angular spectra and we have fitted all the data simultaneously. The data have been analyzed using CompleteEASE 4.1 software.

### 3. Results and discussion

#### 3.1. Thermal properties

In a glass of composition of 70TeO$_2$−5M$_x$O$_y$−10P$_2$O$_5$−10ZnO−5PbF$_2$ in mol%, where M$_x$O$_y$ = (WO$_3$, Nb$_2$O$_5$) doped with 2400 ppm Er$_2$O$_3$, presented in this study, tellurium oxide is a dominant component which plays the vital role as a conditional glass former. A chemical compound such as lead fluoride was added in order to tune specific properties such as minimization of OH$^-$ content and improvement of thermal stability, respectively. ZnO is responsible for the depolymerization of the amorphous glass structure by increas-
ing TeO₃ units. By contribution of the network, former P₂O₅ several advantages are to be expected, e.g. low melting and softening temperatures and high UV transmission. Moreover, the presence of P₂O₅ makes glasses more suitable for RE doping.

The prepared fluorotellurite glasses have different colors ranging from yellowish to greenish depending on the kind of modifiers. All glass obtained were transparent and homogenous, and amorphous, according to XRD data. The prepared samples were air bubbles free and, based on the visual inspection, the defects were not observed. The results of the glass densities measurements are presented in Table 2. Measurements have been made for the variation of the densities of the two glass systems with different modifiers, i.e. 5 mol% of Nb₂O₅ and 5 mol% of WO₃ (glasses M4 and M7, respectively) at the expense of 5 mol% TeO₂ (glass M10). Their densities were found to vary in the range 5.13–5.34 g/cm³. From Table 2 it is clear that the replacement of TeO₂ with WO₃ or Nb₂O₅ has a strong influence on the thermal stability, crystallization temperature Tₓ as well as T₉ that shifts significantly to higher temperatures (Fig. 1).

The glass transition temperature is ranged from 343 to 366°C. It is noticed that the value of T₉ increases by replacing TeO₂ with WO₃ and Nb₂O₅ modifiers, that may be due to the high strength of the bonds. The glass formation process is treated taking into account bound strength considerations. Usually in inorganic chemistry, Pauling’s electronegativity and ionicity values are universally accepted as standardised characteristics of bonds and chemical interactions of atoms. We would like to explain the changes in the glass transition temperature values with use of similar factors charac-

Table 2. Thermal characteristic of glasses (T₉ – glass transition temperature, ΔCₚ – the specific heat, Tₓ – the onset of crystallization temperature, and Tₘ – melting point).

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<tr>
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<td>366</td>
<td>0.159</td>
<td>504</td>
<td>32</td>
<td>138</td>
<td>1.40</td>
<td>602</td>
<td>5.4222</td>
</tr>
</tbody>
</table>

Fig. 1. DSC curves of glasses obtained.
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The effective nuclear charge of an atom, defined as $Z_{\text{eff}} = \sqrt{I'}_v$, where $I'_v$ is the ionisation energy in the Rydberg units, is needed to remove the valence electrons from an atom. Its value is closely related to Pauling’s electronegativity. The relative difference of the nuclear charge of the two bonding atoms constitutes the factor determining the ionicity of the heteropolar bond. According to the Görlich scale [17], the ionicity $i_G$ value of the bonds of the component atoms with oxygen is a parameter characterizing the strength of the bonds which increases with decreasing ionicity. The ionicity $i_G$ or asymmetry of the chemical bonds between different atomic cores or ions, in a cation-oxygen bond, is measured by the relation $i_G = 1 - Z_{\text{eff}1}/Z_{\text{eff}2}$, where $Z_{\text{eff}1} < Z_{\text{eff}2}$. Intrinsic affinity between two different atoms forming a heteronuclear compound is directly connected with the value of ionicity of a chemical bond [18]. At the same time, the localization of the bonding electron $L = \frac{Z_{\text{eff}}}{Z_{\text{eff}1} Z_{\text{eff}2}}^{1/2}$ is assumed as a measure of the rigidity of the bonds. As $Z_{\text{eff}}$ values describe the degree of localization of the bonding electrons, we may use for it the symbol $L = \text{localization}$. The value of $L$ increases with the covalence of the bonds with oxygen [17, 18]. This parameter has been accepted as a measure of the rigidity of the bonds. The ionic character of W–O bonds ($i_G = 0.410$, $L = 2.447$), Nb–O bonds ($i_G = 0.395$, $L = 2.479$) replacing the covalent bonds such as Te–O bonds ($i_G = 0.285$, $L = 2.696$) made the glass structure less rigid, the consequence of which was a decreased stress in the glass. Its relaxation required more energy and hence higher $T_g$ value with the substitution of modifiers (WO$_3$, Nb$_2$O$_5$) in the structure of glasses. The lower $T_g$ value for M10 glass compared with that for M4 and M7 glasses indicates that the glass networks formed by these systems are stronger than those of M10 glass; this confirms the role of transition metal oxides Nb$_2$O$_5$ and WO$_3$ in forming the glass series as conditional glass network formers, as well as the role of the modifiers in forming a stable glass network [19]. The addition of WO$_3$ and Nb$_2$O$_5$ oxides to the glass structure produces complementary effects on magnitude of $\Delta C_p$. As a result of structure depolymerization, the viscosity of the melt increases. Based on DTA curves, it can be found that the onset crystallization temperature is shifted towards higher temperatures and its enthalpy $\Delta H_n$ becomes reduced. This is the evidence of the decreasing ability of the glass for crystallization, manifested by increased values of the index of thermal stability of the glass $\Delta T = (T_n - T_g)$ [20, 21]. Moreover, the Hruby parameter $K_H$, calculated for M4 and M7 glasses, increases in comparison with $K_H$ for M10 glass, confirming thus their higher stability against crystallization. The thermal stability values of glass M4 ($\Delta T = 138$) and glass M7 ($\Delta T = 128$) modified with Nb$_2$O$_5$ and WO$_3$ have similar values in comparison to the thermal stability values for the glass from the P$_2$O$_5$–ZnO–BaF$_2$–K$_2$TeO$_3$–Al$_2$O$_3$–Nb$_2$O$_5$–Er$_2$O$_3$ system presented in [22]. On the other hand, it should be noted that the same glass matrix 70TeO$_2$–5M$_x$O$_y$–10P$_2$O$_5$–10ZnO–5PbF$_2$ in mol%, where M$_x$O$_y$ = (SrO, BaO,
MgO) doped with 600 ppm Er₂O₃ reveals much lower thermal stability values (ΔT = 105, 106, 110) [23].

3.2. Optical properties

The aims of this part of the study were to assess the effect of the glass composition on the optical properties, namely the infrared (IR) transmission and refractive index of selected tellurite glasses. It is to be expected that the addition of WO₃ and Nb₂O₅ oxides to the TeO₂–P₂O₅–ZnO–PbF₂ glass structure can effectively enhance the optical properties. In Fig. 2 we present transmission and reflection spectra of all tested glasses.

The transmission for the niobium oxide sample is the largest in the range from 300 to 2500 nm. Addition of tungsten oxide results in the decrease of transmission com-

Fig. 2. Transmission T and reflection R spectra of tested glasses.

Fig. 3. Dispersion of the refractive index n of fluorotellurite glasses.
pared to the basic glass. Small peaks that are seen in the spectra are due to the presence of erbium ions in the glasses.

The ellipsometric measurements have allowed one to determine the dispersion of the refractive index $n$ of the investigated glasses (Fig. 3).

There are many factors which have very important effects on the refractive index, such as density, polarizability of the first neighbor ions coordinated with it (anion), coordination number of the ion, electronic polarizability of the oxide ion, and optical basicity [24].

The refractive index of fluorotellurite glasses obtained is not lower than 2.0 in the range of 300–1700 nm. By incorporation of $\text{WO}_3$ or $\text{Nb}_2\text{O}_5$ oxides to the $\text{TeO}_2$–$\text{P}_2\text{O}_5$–$\text{ZnO}$–$\text{PbF}_2$ glass matrix, that greatly improves the thermal stability, the values of $n$ slightly increased. Moreover, a linear correlation between $n$ and density $\rho$ is observed. The glass with composition $70\text{TeO}_2$–$5\text{Nb}_2\text{O}_5$–$10\text{P}_2\text{O}_5$–$10\text{ZnO}$–$5\text{PbF}_2$ (M4) has the highest value of the density ($\rho = 5.422$ g/cm$^3$) and the glass $70\text{TeO}_2$–$5\text{WO}_3$–$10\text{P}_2\text{O}_5$–$10\text{ZnO}$–$5\text{PbF}_2$ (M7) has a slightly lower value of the density (5.338 g/cm$^3$). Otherwise, $75\text{TeO}_2$–$10\text{P}_2\text{O}_5$–$10\text{ZnO}$–$5\text{PbF}_2$ (M10) has the lowest value of density ($\rho = 5.260$ g/cm$^3$). This change of density runs parallel to the change in the atomic mass of the modifier. The values of the refractive index $n$, density $\rho$, molar volume $V_m$, oxygen packing density (OPD), molar refraction $R_m$ and the molar polarizability $\alpha_m$ are given in Table 3. The electronic polarizability of the glasses was evaluated using the following Lorentz–Lorenz equation giving the relationship between the molar refraction, the refractive index and density:

$$R_m = \left(\frac{n^2 - 1}{n^2 + 2}\right)V_m$$

Table 3. Values of the refractive index $n$, density $\rho$, molar volume $V_m$, oxygen packing density (OPD), molar refraction $R_m$ and the molar polarizability $\alpha_m$.

<table>
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<tr>
<th>Sample</th>
<th>Modifier type</th>
<th>$\rho$ [g/cm$^3$]</th>
<th>$V_m$ [cm$^3$]</th>
<th>$V_o$ [cm$^3$/mol]</th>
<th>OPD</th>
<th>$\lambda$ [nm]</th>
<th>$n$</th>
<th>$\alpha_m$</th>
<th>$\alpha_m/V_m$</th>
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<tr>
<td>M4</td>
<td>$\text{Nb}_2\text{O}_5$</td>
<td>5.4222</td>
<td>29.430</td>
<td>13.079</td>
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where $V_m$ is the molar volume which is equal to

$$V_m = \frac{\sum x_i M_i}{\rho_{\text{glass}}}$$

(2)

where $M_i$ is the molecular weight of the $i$-th component, $x_i$ is the molar fraction of the $i$-th component and $\rho_{\text{glass}}$ is the glass density.

Molar refraction $R_m$ and refractive index $n$ depend on polarizability $\alpha$ of the material by the sum of $R_1$ and $R_m$ and are proportional to $\alpha$ as follows:

$$\alpha_m = \frac{3 R_m}{4 \pi N_A}$$

(3)

where $\alpha_m$ is the molar polarizability of glass and $N_A$ is the Avogadro number.

The oxygen molar volume $V_o$ has been calculated by the following expression:

$$V_o = \frac{\sum x_i M_i}{\rho_{\text{glass}}} \frac{1}{\sum x_i n_i}$$

(4)

where $n_i$ is the number of oxygen atoms in each oxide.

From this data, it has to be noted that the value of $R_m$ of the prepared glasses is in the range 18.393–19.319 cm$^3$ and $\alpha_m$ is in the range 6.249–6.347 at 435.8 nm. These values are slightly lower than the values of 75TeO$_2$–5WO$_3$–15Nb$_2$O$_5$–5M$_{x}$O$_y$ glasses presented in [24] but, on the other hand, higher that those calculated for $x$RO–(100 – $x$)TeO$_2$ glasses [25]. Sample A with modifier CuO has the highest values of $R_m$ and $\alpha_m$, whereas sample H with modifier Na$_2$O has the lowest values of $R_m$ and $\alpha_m$.

In contradiction to the data presented in [24], the change in $V_o$ values runs parallel to the change in the density value, but the value of $V_m$ indeed is reduced along with a reduction in density, but the changes are not proportional. The changes in $V_m$ and $V_o$ values must be considered by taking into account the molecular weight of constituents in the glass composition, the number of oxygen atoms and bond length, and the cation radius and coordination number. The glass with addition of Nb$_2$O$_5$ has the highest values of $V_m$ and $\alpha_m$ in comparison to the glass with WO$_3$ addition, due to the fact that Nb$_2$O$_5$ has higher molecular weight. The molar volume $V_m$ values exhibits an increase with modifier addition at the expense of TeO$_2$ oxide. This result is due to the increase in the percentage of oxygen atoms which have the highest ionic radius in the glass structure. The oxygen packing density was calculated using the following expression [26]:

$$\text{OPD} = 1000 \rho_{\text{glass}} \frac{\sum x_i n_i}{\sum x_i M_i}$$

(5)

As shown in Table 3, the oxygen molar volume and oxygen packing density values show opposite behavior to each other. Therefore, it can be concluded that, due to the
substitution of lower field intensity constituent ion Te⁴⁺ (1.40) with higher field intensity W⁶⁺ (1.47), a decrease in the oxygen molar volume and an increase in the oxygen packing density values are observed. This also results in high tightly packing of the glass network [27–29].

The molar polarizability of oxide ions is another factor affecting the refractive index value of the prepared glasses. The values of the molar polarizability obtained are shown in Table 3.

The relatively large refractive index of the tellurium niobate glasses is attributed to the hyper polarizability of Nb–O bonds [30]. The more polarizable the outer electrons, the higher $n$.

4. Conclusion

For all investigated glasses, the parameter $\Delta T = (T_n - T_g)$ is within the range from 90 to 137°C, indicating that the thermal stability against crystallization is very high. The addition of Nb₂O₅ and WO₃ is desirable to obtain a wide working temperature range for fiber drawing operation.

The refractive index of fluorotellurite glasses obtained is not lower than 2.0 in the range of 300–1700 nm. Addition of niobium oxide (Nb₂O₅) and tungsten oxide (WO₃) slightly raised the refractive index.

The transmission for the niobium oxide sample is the largest in the range from 300 to 2500 nm. Addition of tungsten oxide results in the decrease in transmission compared to the basic glass.

The glass with addition of Nb₂O₅ has the highest values of $V_m$ (molar volume of the glasses) and $V_o$ (oxygen molar volume) in comparison to the glass with WO₃ addition, due to the fact that Nb₂O₅ has higher molecular weight.

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