Effect of ZnO and Bi$_2$O$_3$ addition on linear and non-linear optical properties of tellurite glasses

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Abstract

Glasses in the system TeO$_2$–Bi$_2$O$_3$–ZnO were studied with respect to their linear refractive indices and optical absorption in the UV–vis range. The third order non-linear refractive indices were measured using degenerated four wave mixing (DFWM). The optical Kerr susceptibilities calculated hereof were in the range from 5.49 to $6.58 \times 10^{-13}$ esu and hence 34–41 times larger than that of fused SiO$_2$. They are roughly proportional to values theoretically calculated by the theory of Lines. © 2006 Elsevier B.V. All rights reserved.

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1. Introduction

In the two past decades, tellurite glasses have attracted a great deal of interest [1–7], due to their potential use as fiber amplifiers and non-linear optical devices [3–7]. The latter is caused by the high non-linear refractive index.

For the determination of non-linear refractive indices, various methods such as three wave mixing, four wave mixing and $z$-scan have been used [1].

The linear refractive indices of tellurite glasses are also notably large and usually in the range from 1.95 to 2.3 [2,8]. While pure TeO$_2$ can only be obtained by rapid quenching, e.g. by twin roller techniques, binary or multi-nary TeO$_2$-based glasses exhibit fairly large glass forming ranges. Especially glasses containing heavy metal oxides have been reported to possess a high degree of optical non-linearity [2–7]. The addition of highly polarizable components, such as Nb$_2$O$_5$ or PbO increases the optical non-linearity. It was reported that such additions lead to remarkable changes in the physical, especially the optical properties [4]. For example the electron phonon interaction [9] gives a contribution to the third order optical susceptibility in ternary tellurium containing glasses.

Tellurite glasses, therefore, are regarded as promising optical materials for up conversion laser and non-linear optical materials, which exhibit high third order non-linear optical susceptibilities [3–6].

This paper provides a study on the preparation and the linear as well as non-linear optical properties of glasses in the system TeO$_2$/Bi$_2$O$_3$/ZnO.

2. Theory

Generally, the polarization, $P$, of a material at high light intensities is given by

$$P = \sum_{n=1}^{\infty} \chi^{(n)} \cdot E \quad (1)$$
with $E$ = electric field and $\chi^{(n)}$ the $n$th order optical susceptibility tensors.

For an isotropic medium, $\chi^{(2)}$ is zero, and $\chi^{(3)}$ is given by

$$\chi^{(3)}(\omega; \omega_1, \omega_2, \omega_3) = N \cdot f(\omega_1) \cdot f(\omega_2) \cdot f(\omega_3) \cdot \gamma(\omega; \omega_1, \omega_2, \omega_3)$$

with $\omega = \omega_1 + \omega_2 + \omega_3$, $N$ is the particle density, $f(\omega_n)$ are the local field vectors and $\gamma(\omega; \omega_1, \omega_2, \omega_3)$ is the second molecular hyperpolarizability. The Kerr susceptibility $\chi^{(3)}$ is related to the non-linear refractive index defined by

$$n = n_0 + n_2 I,$$

$$n = n_0 + n_2 |E|^2$$

with $n_0$ = linear refractive index, $I$ = light intensity and $|\rangle$ denotes the time average. The non-linear refractive index $n_2$ in SI units can be transferred into $n_2$ in cgs system:

$$n_2 \left[ \frac{m^2}{\omega} \right] = \frac{40 \pi}{c n_0} n_2 \ [\text{esu}]$$

with $c$ = speed of light ($3 \times 10^8$ m/s).

The optical Kerr susceptibility $\chi^{(3)}$ is related to both the linear, $n$, and the non-linear refractive indices, $n_2$:

$$\chi^{(3)} \ [\text{esu}] = \frac{n_0}{3\pi} n_2 \ [\text{esu}].$$

### 3. Experimental

Glasses with the compositions (95 $- \chi$)TeO$_2$ $\cdot$ 5Bi$_2$O$_3$ $\cdot$ xZnO ($\chi =$ 15, 20 and 25) and 90TeO$_2$ $\cdot$ 10Bi$_2$O$_3$ $\cdot$ xZnO ($\chi =$ 15, 20 and 25) were prepared from reagent grade TeO$_2$ (99.999, Ferak), Bi$_2$O$_3$ (99.9, Merck) and ZnO (99.5, Chemaplot). The batches were placed in a gold crucible and then cast in a graphite mould. Subsequently, the samples were transferred to an annealing furnace and kept at 250°C for 2 h. The furnace was then switched off and allowed to cool. From the glassy samples, prisms of the dimension 30 $\times$ 15 $\times$ 15 mm$^3$ were cut. The prisms were ground and polished using water as a liquid component. The prisms were used to measure the linear refractive indices at wavelengths of 643.8, 589.3, 546.1, 479.98 and 435.8 nm using a precision goniometer (SGO 1.1, Präzisionsmchanik Freiberg, Germany). The accuracy of the measurement is ±1 x 10$^{-5}$.

To measure non-linear refractive indices as well as absorption spectra, flat samples with a thickness of 1 mm were prepared. Degenerate four-wave mixing (DFWM) was applied to measure $n_2$. The experimental setup used has already been described in Ref. [10]. A Ti sapphire laser system delivering 150 fs pulses of a wavelength of 800 nm was used. The pulse energies were in the range from 3 to 4 µJ with a repetition rate of 10 s$^{-1}$. Due to the small repetition rates and the short duration of the pulses, thermo optical effects are negligible. The DFWM setup used tunable laser splitters, each of them consisted of a rotatory half-wave plate and a glan prism. This enables an easy adjustment of the intensities of the three pump beams. Two of the pump beams were sent through delay stages. The first served to adjust the temporal overlap of two of the pump beams, whereas the second delay stage was tuned to set the third pump beam to a delay $\Delta t$ in relation to the other two pulses. The three beams were focused onto the sample by a lens with the focal length of 12.5 cm. The angle between the pump beams was 4°. All three beams had approximately the same intensity and were linearly polarized in the same direction. For each time delay, the measured signals were averaged over at least 30 laser pulses. In order to minimize the effect of pulse energy fluctuations, for each pulse, the DFWM signal was divided by a reference signal obtained by a reference detector measuring the pulse energy. For a Kerr like non-linearity and negligible absorption in the sample at the respective wavelength, the maximum DFWM signal intensity, $I_{\text{DFWM}}$, is given by [11]:

$$I_{\text{DFWM}} = \text{const} \left| \chi^{(3)} \right|^2 L^2 I^3 = \text{const} |n_2|^2 L^2 I^3$$

with $I$ = intensity of the pump beams, $L$ = length of the sample; the constant depends on the used definitions.

The signal intensity depends on $|n_2|^2$ and hence no statement on the sign of $n_2$ is possible. The signal intensity was referenced to a fused silica plate with a thickness of 517 µm, the $|n_2|^2$ values were calculated using Eq. (8):

$$\frac{|n_2(\text{sample})|}{|n_2(\text{ref.})|} = \sqrt{\frac{I_{\text{DFWM(sample)}}}{I_{\text{DFWM(ref.)}}}} \times \frac{L(\text{ref.})}{L(\text{sample})} \left( 1 - R(\text{ref.}) \right)^2 \left( 1 - R(\text{sample}) \right)^2.$$

The last term in Eq. (8) introduces a correction of the reflection losses at the samples and reference surfaces (which are notably different for tellurite glass and fused silica). The reflectivity $R$ was calculated from the linear refractive indices using Fresnel equation. The non-linear refractive index $n_2$ of fused silica was assumed to be $3 \times 10^{-16}$ cm$^2$/W [11].

Absorption spectra were recorded in the wavelength range from 200 to 3200 nm using a Shimadzu 3101PC spectrometer at samples with thicknesses of 1 and 11 mm. The 1 mm sample was located in the reference beam in order to eliminate reflection losses which depend on the linear refractive index. The densities were measured by a helium pycnometer (AccuPyc 1330) with an accuracy of ±0.03%.

### 4. Results

The densities of the as prepared glasses are summarized in Table 1, column 5. They are all in the range from 5.87 to 6.27 g x cm$^{-3}$. The density increases with increasing Bi$_2$O$_3$ and ZnO concentrations. The linear refractive indices measured for various wavelengths as well as the Abbe numbers...
calculated hereof are summarized in Table 1, columns 6–11. The refractive indices are in the range from 2.1 to 2.275 and increase with increasing Bi$_2$O$_3$ and decreasing ZnO concentrations. The Abbe numbers $v_e = (n_C - 1) / (n_F - n_C)$ are in the range from 16.9 to 18.

Fig. 1 shows a plot of $(\alpha h)^{1/2}$ versus $h \alpha$ (with $\alpha =$ polarizability) for all glasses studied. From the linear correlations observed, the optical band gap energy, $E_g$, can be calculated from Tauc equation [12]:

$$\alpha(\alpha) = \frac{(h \alpha - E_g)^2}{h \alpha}.$$  \hspace{1cm} (9)

The optical band gap energies, $E_g$, lie in the range from 2.57 to 2.63 eV. In Fig. 2, a plot $\ln(\alpha)$ versus $h \alpha$ is shown. The observed linear correlations enable the calculation of Urbach energies, $\Delta E$ [13]:

$$\ln(\alpha) = \frac{h \alpha}{\Delta E}.$$ \hspace{1cm} (10)

Optical band gap energies, $E_g$ and Urbach energies are summarized in Table 2, columns 2 and 3, respectively.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Composition</th>
<th>Density in g/cm$^3$</th>
<th>Linear refractive indices at 643.8 nm</th>
<th>Linear refractive indices at 589.3 nm</th>
<th>Linear refractive indices at 546.06 nm</th>
<th>Linear refractive indices at 479.98 nm</th>
<th>Linear refractive indices at 435.8 nm</th>
<th>Abbe number $v_d$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>80 5 15</td>
<td>5.870</td>
<td>2.1387</td>
<td>2.1543</td>
<td>2.1698</td>
<td>2.2064</td>
<td>2.2452</td>
<td>±0.0002</td>
</tr>
<tr>
<td>B</td>
<td>75 5 20</td>
<td>5.898</td>
<td>2.109</td>
<td>2.136</td>
<td>2.151</td>
<td>2.1861</td>
<td>2.234</td>
<td>±0.00</td>
</tr>
<tr>
<td>C</td>
<td>70 5 25</td>
<td>5.951</td>
<td>2.103</td>
<td>2.118</td>
<td>2.131</td>
<td>2.165</td>
<td>2.201</td>
<td>±0.001</td>
</tr>
<tr>
<td>D</td>
<td>75 10 15</td>
<td>6.090</td>
<td>2.161</td>
<td>2.178</td>
<td>2.195</td>
<td>2.234</td>
<td>2.275</td>
<td>±0.00</td>
</tr>
<tr>
<td>E</td>
<td>70 10 20</td>
<td>6.160</td>
<td>2.1452</td>
<td>2.1612</td>
<td>2.1773</td>
<td>2.2149</td>
<td>2.2554</td>
<td>±0.0002</td>
</tr>
<tr>
<td>F</td>
<td>70 10 25</td>
<td>6.267</td>
<td>2.1284</td>
<td>2.144</td>
<td>2.1596</td>
<td>2.196</td>
<td>2.235</td>
<td>±0.001</td>
</tr>
</tbody>
</table>

Error in density: ±0.001.
is fast in comparison to the duration of the laser pulses. The signal intensity of the tellurite glasses is 250–300 times larger than that of fused silica. In Table 3, column 2, non-linear refractive indices which were calculated from the DFWM signals using Eq. (7) are shown (|\(n_2|\) values using Eq. (6) are summarized.

5. Discussion

The dependency of the linear refractive index on the photon energy, \(E = h\nu\), can be described by the Sellmeier gap energy, \(E_S\), and the dispersion energy, \(E_d\) [5,14]:

\[
\frac{1}{n^2(E) - 1} = \frac{E^2}{E_S} - \frac{E^2}{E_S \cdot E_d}.
\]

(11)

Fig. 3 shows a plot of \(1/(n^2(E) - 1)\) versus \(E^2\) for the samples studied. From the linear regression, values of \(E_S\) and \(E_d\) are obtained. They are summarized in Table 2, columns 4 and 5. The values of \(E_S\) are in the range from 6.33 to 6.63 eV and those of \(E_d\) in the range from 20.69 to 21.06 eV. The values for both \(E_S\) and \(E_d\) are in a fairly narrow range and do not vary systematically with composition.

In the plot \((\sqrt{h\nu})^{1/2}\) versus \(h\nu\) (see Fig. 1), linear correlations were observed for all glasses studied. This is evidence for a direct transition responsible for the UV cut-off. The optical band gap energies calculated from this plot are in the range from 2.57 to 2.63 eV. Optical band gap energies reported in the literature are mostly in the range of 2.8–3.5 eV [15–19]. For binary \(\text{TeO}_2–\text{WO}_3\) [17], \(\text{TeO}_2–\text{ZnO}\) and \(\text{TeO}_2–\text{Nb}_2\text{O}_5\) [18] glasses values of around 3.45 and 3.1 eV were respectively obtained. Adding alkali oxides to the \(\text{TeO}_2–\text{Nb}_2\text{O}_5\) glasses resulted in a decrease of the optical band gap energies of 2.7–3 and 3.1–3.3 for \(\text{Na}_2\text{O}\) [16] and \(\text{Li}_2\text{O}\) [18], respectively. The optical band gap energies of the studied \(\text{TeO}_2–\text{Bi}_2\text{O}_3–\text{ZnO}\) system are hence smaller than those reported up to now in the literature for comparable tellurite glasses. By analogy, the values for the...
Urbach energy which are in the range from 0.054 to 0.066 eV are smaller than reported for other glass systems, such as TeO$_2$–Na$_2$O–Nb$_2$O$_5$ [19], TeO$_2$–Nb$_2$O$_5$ [20] or TeO$_2$–PbO [21]. The Urbach energy is caused by the band tails associated with the valence and conduction bands extending into the band gap. This is attributed to the fluctuation of internal fields due to the disordered structure in non-crystalline materials. Here, the Urbach energy corresponds to the width of localized states and hence is a measure for the disorder in amorphous solids. Glasses with smaller Urbach energies hence have a smaller tendency for the disorder in amorphous solids. Glasses with non-crystalline materials. Here, the Urbach energy correlates with the width of localized states and hence is a measure for the disorder in amorphous solids. Glasses with smaller Urbach energies hence have a smaller tendency for bond rupture and defect formation [22,23].

According to the theory of Lines [24,25], the non-linear optical susceptibility of metal oxides depend on the linear refractive index, the photon energy of the light used as well as on the Sellmeier gap energy, $E_S$. Additionally, it is affected by the Te–O bond length in the respective glass composition

$$\chi^{(3)} = K \left( \frac{n^2(E) + 2}{3} \right)^3 \frac{(n^2(E) - 1)E^4_S}{(E^2 - E^2)^2} \cdot d^2,$$  

(12)

where $d$ is the metal oxygen bond length and $K$ is 0.26 x 10$^{-12}$ esu eV$^2$ Å$^{-2}$.

According to Kim et al. [5], this concept, developed for crystalline oxides, is also valid for tellurite glasses. Since d is not known exactly, in Table 3 column 4, $\chi^{(3)}/d^2$-values are summarized for the respective glass compositions. Kim et al. [4] inserted as Te–O bond length for glasses in the system La$_2$O$_3$–TeO$_2$: $d = 2.01$ Å which is reported to be equivalent to that of the Te–O bond for the calculation of $\chi^{(3)}$ values.

Fig. 6 shows a plot of the experimental $\chi^{(3)}$ values against the $\chi^{(3)}/d^2$ values, theoretically calculated using Eq. (12). The solid line is a regression line drawn through the origin. The measured $\chi^{(3)}$ values are roughly proportional to the calculated ones. The slope of the drawn regression line is 2.3 Å$^2$. The $\chi^{(3)}$-values measured are 34-41 times larger than that of fused silica.

The variations of the physical properties with the glass composition should be due to the respective glass structure. In principle, the structure of pure TeO$_2$ glass is composed of TeO$_4$ trigonal bipyramids (tp) with two axial positions occupied by oxygens and two oxygens in equatorial positions. The axial Te–O bonds are somewhat longer than the equatorial ones. The third equatorial position is occupied by a lone pair of electrons. If network modifying oxides, such as ZnO are added, non-bridging oxygens are formed and the TeO$_4$ trigonal bipyramids are transferred into TeO$_3$ trigonal pyramids (tp) [25–29]. Here, the lone pair occupies the apex of the sp$^3$ hybrid orbital. The electronic transition which gives rise to the high non-linear refractive index is that from the non-bonding O2p orbital to the empty non-bonding Te5d orbital [15]. The effect of conditional glass formers, such as WO$_3$ or V$_2$O$_5$ is reported to be qualitatively the same as that of network modifiers, however, the effect is not as pronounced [30,31]. From wide angle X-ray and neutron scattering, it is known from different systems, such as TeO$_2$/V$_2$O$_5$ [28] or TeO$_2$/Nb$_2$O$_5$/ZnO [29], that the Te–O bond lengths are different; one Te–O bond is shorter (1.9 Å) than the other two or three Te–O bonds (2–2.1 Å).

The formation of non-bridging oxygen by introducing ZnO is also seen in the increase in density, which is evidence for a more compact glass structure. With increasing ZnO concentration, the linear refractive index decreases for all glasses studied. The non-linear refractive index remains the same within the limits of error (5 mol% Bi$_2$O$_3$) or increases (10 mol% Bi$_2$O$_3$). Since the density of the glass increases, the decrease in the linear refractive index should be due to the low polarizability of Zn$^{2+}$. Increasing the Bi$_2$O$_3$ concentration from 5 to 10 mol% results in a notable increase in the density, the linear and non-linear refractive indices. This is caused by the high polarizability of the Bi$^{3+}$ ion. However, as noted above, the increase in the Bi$_2$O$_3$ concentration should also result in the transfer of TeO$_4$ trigonal bipyramids into TeO$_3$ trigonal pyramids. Since this effect should be more pronounced in the case of ZnO (as noted above), it is supposedly not responsible for the increase in the non-linear refractive indices. It should be noted that the effect of increasing ZnO and Bi$_2$O$_3$ concentrations is also seen in the $\chi^{(3)}/d^2$ values calculated by Eq. (12) (see Table 3, column 4).

In principle, the slope of the regression line in Fig. 6 enables the calculation of the Te–O bond length. The result of this calculation ($d = 1.52$ Å), however, is not within the range, Te–O bond lengths are expected. As mentioned above, Kim et al. assumed a Te–O bond length of 2.01 Å and inserted this bond length into Lines equation. The length of the Bi–O bond is around 2.4 Å, while that of the Zn–O bond was reported to be 2.03 and 2.15 Å for four and sixfold coordination, respectively. Hence, the variation of the bond lengths is comparably small (2.20 ± 0.2 Å) and...
all Me–O bonds occurring in the investigated glass are far larger than 1.52 Å.

In this context, it should be noted that \( \chi^{(3)} \) can only roughly be estimated from Eq. (12). In our case there seems to be a systematic error. Assuming a more realistic Te–O bond length of 1.9 Å, the calculated \( \chi^{(3)} \)-values are in the average around 57% larger than the measured ones. As recently noted, also the wavelength dependency of \( \chi^{(3)} \) is not correctly given by Eq. (12) [10] as illustrated for the system TeO2–WO3–ZnF2.

6. Conclusions

The studied TeO2–Bi2O3–ZnO system shows high linear refractive indices in the range of 2.1–2.25. The experimental Kerr susceptibilities are in the range of 5.49–6.58 \( \times 10^{-13} \) esu. They increase with increasing Bi2O3 concentration. Kerr susceptibilities calculated with Lines’ equation are more than 50% larger than the experimentally determined ones. The studied glasses show optical band gap energies in the range from 2.57 to 2.63 eV and Urbach energies which lie between 0.054 and 0.066 eV. Both optical band gap and Urbach energy are smaller than for other glass systems reported in the literature up to now. This indicates low defect concentrations.

References