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<th>Nonlinear Optical Properties of TeO₂-Based Glasses: RO-TeO₂ (R=Mg, Sr and Ba) Binary Glasses (Commemoration Issue Dedicated to Professor Sumio Sakka On the Occasion of His Retirement)</th>
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Kyoto University
Nonlinear Optical Properties of TeO₂-Based Glasses: RO-TeO₂ (R=Mg, Sr and Ba) Binary Glasses

Sae-Hoon Kim*, Toshinobu Yoko* and Sumio Sakka*

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The third-order nonlinear optical susceptibilities, $\chi^{(3)}$, of $x\text{RO}(100-x)\text{TeO}_2$ (R=Mg, Sr and Ba) binary glasses have been measured with a special attention to the effect of addition of second component using the third harmonic generation (THG) method. The $\chi^{(3)}$ value obtained is for example, $9 \times 10^{-13}$ esu for 10BaO:90TeO₂ glass. It is found that the third-order nonlinear optical susceptibilities $\chi^{(3)}$ of alkaline-earth oxide containing TeO₂ glasses decrease drastically with increasing alkaline-earth oxide content, corresponding to the decrease in the polarizability in unit volume. An excellent linear relationship is found to hold between the $\chi^{(3)}$ and $(n_0^2+2)^3(n_0^2-1)E_d/E_0^5$ irrespective of kind of alkaline earth metals.

KEY WORDS: Third-order nonlinear optical susceptibilities/$\chi^{(3)}/$ Alkaline-earth oxide containing TeO₂ glasses

1. INTRODUCTION

TeO₂-based glasses have attracted much attention as photonic materials.¹⁻³ TeO₂ itself has been found to be a superior photonic material having a large $\chi^{(3)}$ value of $1.4 \times 10^{-12}$ esu.⁴ The problem of this glass is that only a small piece of glass is produced even by a rapid quenching technique. Therefore, it is absolutely required to add second components in order to obtain a large piece of glass. Fortunately, TeO₂ is known to form a glass with a variety of metal oxides and halides over a relatively wide composition range.⁵⁻⁶

In this respect, it is of essence to investigate the influence of addition of each second component on the nonlinear optical properties of TeO₂-based glasses in order to develop glass materials applicable to photonic devices. In this paper, we will deal with the effect of alkaline earth oxide as a second component. Especially, the relationship between $\chi^{(3)}$ and optical parameters is discussed on the basis of semiempirical formula.

2. EXPERIMENTALS

The batch compositions of the binary xRO-(100-x)TeO₂ (R=Mg, Sr and Ba) glasses prepared in this study are shown in Table 1. A 10 g batch of well mixed oxides was melted in a Pt-5% Au crucible at 700–800°C in an ambient atmosphere. The melts were poured into a brass mold and quenched to room temperature. After annealing at 200°C, the glasses were cut into a plate of $10 \times 10 \times 2$ mm³ in size. Both faces were optically polished to eliminate a light scattering.

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Table 1. Nonlinear optical properties of xRO-(100−x)TeO₂ (R=Mg, Sr and Ba) binary glasses.

<table>
<thead>
<tr>
<th>Glass</th>
<th>Density /gcm⁻³</th>
<th>n₁</th>
<th>n₃</th>
<th>E_d /eV</th>
<th>E₄ /eV</th>
<th>R_m/V_m</th>
<th>l_c /μm</th>
<th>T₃₉⁸ /%</th>
<th>T₇₆⁰ /%</th>
<th>I₃₉⁸,Sample /10⁻⁸esu</th>
<th>K /10⁻¹⁰esu³</th>
</tr>
</thead>
<tbody>
<tr>
<td>xMgO (100−x)TeO₂ glasses</td>
<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>x=10</td>
<td>5.380</td>
<td>2.050</td>
<td>2.106</td>
<td>7.12</td>
<td>22.6</td>
<td>0.516</td>
<td>5.66</td>
<td>79.9</td>
<td>85.7</td>
<td>5.8</td>
<td>5.46</td>
</tr>
<tr>
<td>x=15</td>
<td>5.315</td>
<td>2.010</td>
<td>2.063</td>
<td>7.31</td>
<td>22.0</td>
<td>0.503</td>
<td>5.98</td>
<td>82.0</td>
<td>87.5</td>
<td>5.1</td>
<td>4.45</td>
</tr>
<tr>
<td>x=20</td>
<td>5.202</td>
<td>2.003</td>
<td>2.053</td>
<td>7.34</td>
<td>21.9</td>
<td>0.501</td>
<td>6.33</td>
<td>79.2</td>
<td>85.3</td>
<td>4.0</td>
<td>3.90</td>
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<tr>
<td>xSrO (100−x)TeO₂ glasses</td>
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<tr>
<td>x=10</td>
<td>5.528</td>
<td>2.054</td>
<td>2.118</td>
<td>6.75</td>
<td>21.5</td>
<td>0.518</td>
<td>4.95</td>
<td>74.1</td>
<td>75.9</td>
<td>6.0</td>
<td>7.95</td>
</tr>
<tr>
<td>x=15</td>
<td>5.434</td>
<td>2.015</td>
<td>2.073</td>
<td>6.92</td>
<td>20.9</td>
<td>0.505</td>
<td>5.46</td>
<td>74.3</td>
<td>77.4</td>
<td>4.9</td>
<td>6.11</td>
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<tr>
<td>xBaO (100−x)TeO₂ glasses</td>
<td></td>
<td></td>
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<tr>
<td>x=10</td>
<td>5.593</td>
<td>2.055</td>
<td>2.119</td>
<td>6.71</td>
<td>21.4</td>
<td>0.518</td>
<td>4.95</td>
<td>78.9</td>
<td>81.2</td>
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<td>9.0</td>
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<tr>
<td>x=15</td>
<td>5.556</td>
<td>2.042</td>
<td>2.106</td>
<td>6.76</td>
<td>21.2</td>
<td>0.556</td>
<td>4.95</td>
<td>79.2</td>
<td>81.0</td>
<td>6.1</td>
<td>6.9</td>
</tr>
<tr>
<td>x=20</td>
<td>5.526</td>
<td>2.006</td>
<td>2.063</td>
<td>6.92</td>
<td>20.8</td>
<td>0.526</td>
<td>5.56</td>
<td>79.3</td>
<td>81.6</td>
<td>6.0</td>
<td>5.8</td>
</tr>
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</table>

at the surface. The thickness of glasses for THG and transmittance measurement was 1.0 ± 0.05 mm.

The refractive index of each glass was measured over a wide wavelength range from 486 to 1,000 nm by Mizojiri Optical Works model DVA-36VW ellipsometer.

Fig. 1. Variation of refractive index with wavelength in xRO-(100−x)TeO₂ (R=Mg, Sr and Ba) binary glasses.
The transmittance of glasses was determined in the wavelength range from 200 to 2,000 nm by a Hitachi model U-3500 spectrophotometer.

The density was measured by the Archimedes method using kerosene as an immersion liquid at 22°C.

The $\chi^{(3)}$ values were determined by the third harmonic generation (THG) method, using a nonlinear optical measurement apparatus assembled by Tokyo Instruments, Inc., Tokyo, Japan. Further details of the THG measurements are described in our previous papers.2'4'7

3. RESULTS

As shown in Fig. 1, the refractive indices $n$ of $xRO\cdot(100-x)TeO_2$ ($R=Mg$, Sr and Ba) binary glasses are plotted as a function of wavelength ranging from 486 to 1,000 nm. In all

![Graphs showing the dependence of refractive index on photon energy for different compositions of binary glasses.](image)

Fig. 2. Dependence of refractive index on photon energy in $xRO\cdot(100-x)TeO_2$ glasses: (a) $R=Mg$ ($x=10, 15$ and $20$), (b) $R=Sr$ ($x=10$ and $15$) and (c) $R=Ba$ ($x=10, 15$ and $20$).
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casees they monotonously decrease with increasing wavelength. Figure 2(a)–(c) show the plots of $1/(n^2-1)$ vs. $E^2$ according to the following equation proposed by Wemple.\(^8\)

\[
\frac{1}{n^2-1} = \frac{E_d}{E_0} - \frac{E^2}{E_dE_0}
\]

(1)

where $E_d$ is the dispersion energy and $E_0$ the excitation energy. Fairly well linear relations between them are observed. The parameters $E_0$ and $E_d$ obtained from these linear relations are tabulated in Table 1.

Figure 3 shows the refractive indices at 1,900 nm ($n_w$) and 633 nm ($n_{3w}$) as a function of RO content. For comparison, the values of $n_w$ and $n_{3w}$ of pure TeO₂ glass are also plotted which are cited from ref. 4. In all cases, the addition of RO to TeO₂ reduces the refractive index of TeO₂ glass in the order, BaO > SrO > MgO.

Figure 4(a) and (b) show the composition dependences of the molar volume $V_m$ obtained from density measurements and the molar refraction $R_m$ defined as,\(^9\)

\[
R_m = V_m \left[ \frac{(n_w^2-1)/(n_w^2+2)}{n_{3w}} \right]
\]

(2)

where $n_w$ is the refractive index. The addition of BaO slightly increases the $V_m$ of TeO₂ glass. The addition of SrO does not seem to change the $V_m$ of TeO₂ glass. The $R_m$'s of TeO₂ decrease with RO content in the order BaO > SrO > MgO. The $R_m/V_m$, which means the polarizability

![Graph 1](image1)

![Graph 2](image2)

Fig. 3. Variation of linear refractive index at 633 nm ($n_w$) and 1,900 nm ($n_{3w}$) with RO (Mg, Sr and Ba) content in RO-TeO₂ binary glasses.
Fig. 4. Composition dependences of (a) Molar volume \( V_m \) and (b) Molar refraction \( R_m \) in \( xRO \cdot (100-x)TeO_2 \) (R=Mg, Sr and Ba) binary glasses.

The third-order nonlinear optical susceptibilities, \( \chi^{(3)} \), determined from the third harmonic generation intensity \( I_{3\omega} \) are shown in Fig. 6. In all cases, the \( \chi^{(3)} \) values decrease with RO content in the order BaO > SrO > MgO.

4. DISCUSSION

The addition of alkaline earth oxides, MgO, SrO and BaO, has been found to decrease both the refractive index and \( \chi^{(3)} \) of TeO_2 glass. It is therefore concluded that although these oxide components have a positive effect in that they extend the glass forming region of TeO_2-based glasses to a considerable extent, they do not improve the linear and nonlinear optical properties of TeO_2-based glasses at all.

Fig. 7 shows a relation between the \( \chi^{(3)} \) and \( n_\omega \). It is interesting to note that the \( \chi^{(3)} \) values are much lower in MgO-TeO_2 glasses than in SrO and BaO-TeO_2 glasses even though their \( n \) values are the same. In the latter two glass systems, they have almost the same \( \chi^{(3)} \) values when the \( n \) values are the same. Figure 8 shows a relation between the \( \chi^{(3)} \) and \( (R_m/V_m)^4 \). Although the \( \chi^{(3)} \) increase with increasing \( (R_m/V_m)^4 \), a unique straight line can not be fitted to the data.
Fig. 5. Polarizability per unit volume \((R_m/V_m)\) of \(x\)RO\((100-x)\)TeO\(_2\) (R = Mg, Sr and Ba) binary glasses as a function of RO content.

Fig. 6. The third-order nonlinear optical susceptibility \(\chi^{(3)}\) of \(x\)RO\((100-x)\)TeO\(_2\) (R = Mg, Sr and Ba) binary glasses as a function of RO content.
indicating that the generalized Miller’s rule\textsuperscript{10,11} does not strictly hold in these glasses. It should be also noted that the MgO-TeO\textsubscript{2} glasses exhibit a different behavior from other glasses just like in Fig. 7.

As stated above, $\chi^{(3)}$ of MgO-TeO\textsubscript{2} glasses is much smaller than that of SrO-TeO\textsubscript{2} and BaO-TeO\textsubscript{2} glasses. This may reflect that MgO-TeO\textsubscript{2} glasses have unit structures different from SrO or BaO-TeO\textsubscript{2} glasses. In fact, Sekiya et al.\textsuperscript{12} reported based on the Raman spectroscopy that the structural units contained in SrO and BaO-TeO\textsubscript{2} glasses are very similar to each other, while those in MgO-TeO\textsubscript{2} glasses are quite different from the case for SrO and BaO-TeO\textsubscript{2} glasses. In SrO- and BaO-TeO\textsubscript{2} glasses, isolated structural units, such as Te\textsubscript{2}O\textsubscript{5}\textsuperscript{2−} and TeO\textsubscript{3}\textsuperscript{2−} ions, coexist with a continuous network composed of tellurium-oxygen polyhedra. In MgO-TeO\textsubscript{2} glasses, the coordination state of tellurium atom changes in analogy with the case of BaO-TeO\textsubscript{2} glasses, but a new structural unit, (Te\textsubscript{3}O\textsubscript{8}\textsuperscript{4−})\textsubscript{n}, found in Pb\textsubscript{2}Te\textsubscript{3}O\textsubscript{8}, Nb\textsubscript{2}Te\textsubscript{3}O\textsubscript{11}, Mg\textsubscript{2}Te\textsubscript{3}O\textsubscript{8} and Zn\textsubscript{2}Te\textsubscript{3}O\textsubscript{8}, is formed in high MgO content glasses.

Figure 9 shows a relation between the $\chi^{(3)}$ and the term $(n_{\omega}^2+2)^2(n_{\omega}^2-1)E_d/E_0^2$\textsuperscript{2,4}, which was originally derived by Lines\textsuperscript{13-14} based on the bond orbital theory\textsuperscript{15-16} and modified by the present authors\textsuperscript{2,4}. A good linear relationship between two is observed. A discrepancy, as in Fig. 7 and 8, is not observed in this case. These means that the relation in Fig. 9 is more universal than the relations between the $\chi^{(3)}$ and $n$ or $(R_m/V_m)^4$, and useful to predict the $\chi^{(3)}$ value from these measurable parameters, $n$, $E_d$ and $E_0$.

5. CONCLUSION

Linear and nonlinear optical properties of $x$RO-(100$-x$)TeO\textsubscript{2} (R=Mg, Sr and Ba) glasses
Nonlinear Optical Properties of TeO₂-Based Glasses

Fig. 8. Relationship between the $\chi^{(3)}$ and $(R_m/V_m)^4$.  

Fig. 9. Relationship between the $\chi^{(3)}$ and the term $(n^2 + 2)^3(n^2 - 1)E_d/E_0^2$.  

(185)
have been measured. The results obtained are summarized as follows.

1. Alkaline earth oxides, such as MgO, SrO and BaO deteriorate both the linear and nonlinear optical properties of TeO₂ glasses, although they extend the glass forming region.

2. The structure of MgO-TeO₂ glasses may possibly be different from that of SrO- and BaO-TeO₂ glasses which have a basically similar structure to each other and both contain isolated structural units of Te₂O₅²⁻ and TeO₃²⁻. The difference in glass network structure is reflected on the linear relationship between the \( \chi^{(3)} \) and linear refractive index or \( \left( \frac{R_m}{V_m} \right)^4 \).

3. The modified Lines relationship, \( \chi^{(3)} \propto \frac{n_m^2 + 2}{n_m^2 - 1} \cdot \frac{E_d}{E_0} \), was found to hold for the alkaline earth tellurite glasses irrespective of the kind of the alkaline earth metal.

Acknowledgement

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REFERENCES