The effect of compositional changes on the physical properties of 40PbO 10Bi₂O₃ (50-0.1)B₂O₃xFeO glass system has been investigated. The physical properties include, density, molar volume, optical electronegativity, optical energy gap, linear refractive index, molar refraction, electronic polarizability, third order nonlinear susceptibility, have been studied theoretically for 40PbO 10Bi₂O₃ (50-0.1)B₂O₃xFeO glass system where (x= 0.2, 0.3, 0.4, 0.5). An analysis of physical parameters related to these compositions was compared with theoretical predictions. It was found that by increasing FeO content, the glass matrix becomes more dense, and the optical energy gap decreases, but the refractive index increases. The electronic polarizability of oxide ion increases with increasing optical basicity. The value of optical basicity shows that the glass materials are more basic. It is suggested that the ability of oxide ion to donate electrons to surrounding cations increases. Also, it was found that the values of third order nonlinear susceptibility increase by increasing FeO content and are found to be larger than those of the silica based glasses. The high values of nonlinear refractive index for all the studied samples are advantageous for all optical signal processing and telecommunications. Also, it was found that the values of third order nonlinear susceptibility increase with decreasing the optical energy gap and increasing the refractive index for all the studied samples. Finally, new nonlinear optical materials were suggested.

Introduction

Nonlinear optics is the study of phenomena that occur as a consequence of the modification of the optical properties of a material system by the presence of light. Dimitrov and Sakka [1] found that the most important factors which govern the nonlinear response of simple oxide are the linear refractive index and the optical energy gap which are related with oxide metallicity. It is suggested that oxides with a high nonlinear refractive index are found to possess a high linear refractive index and a small optical energy gap which has been attributed to the increase of oxide metallicity. The estimation of electronic polarizability of ions is the subject of the so called polarizability approach in material science. The polarizability approach has shown renewed interest because of the need to design optical functional materials and to search for novel glasses with higher optical performance such as oxide glasses with high third order nonlinearities [2]. It is suggested that oxides with a high nonlinear refractive index are found to possess high values of optical basicity and high values of oxide ion polarizability [3-7]. The optical properties of 40PbO 10Bi₂O₃ (50-1) B₂O₃xFeO glass system where (x= 0.2, 0.3, 0.4, 0.5) have been studied [8]. Appropriate amounts (all in mol %) of reagent grades of Bi₂O₃, PbO, H₃BO₃, and FeO powders were thoroughly mixed in an agate mortar and melted in a platinum crucible in the temperature range 950-1000 °C in a PID temperature controlled furnace for about 1 h until a bubble free transparent liquid was formed. The resultant melt was then poured in a brass mould and subsequently annealed at 300 °C. The amorphous state of the glasses was confirmed by X- ray diffraction. The optical absorption spectral studies of PbO Bi₂O₃ B₂O₃FeO glasses [8] indicate the presence of part of iron ions in Fe³⁺ state occupy tetrahedral positions, if FeO is present in lower concentrations; when the concentration of FeO is in higher quantities (> 0.1%), these ions seem to exist in Fe²⁺ state. The aim of the present work is to calculate theoretically the physical properties of 40PbO 10Bi₂O₃ (50-1)B₂O₃xFeO glass system where (x= 0.2, 0.3, 0.4, 0.5) and compare it with the experimental results [8].

Results and Discussion

Density

The density of all the glasses under study can be calculated from the following expression:
\[ d = \left( X_{\text{PbO}} d_{\text{PbO}} + X_{\text{Bi}_2\text{O}_3} d_{\text{Bi}_2\text{O}_3} + X_{\text{B}_2\text{O}_3} d_{\text{B}_2\text{O}_3} + X_{\text{FeO}} d_{\text{FeO}} \right) \]

where, \( X_{\text{PbO}}, X_{\text{Bi}_2\text{O}_3}, X_{\text{B}_2\text{O}_3} \) and \( X_{\text{FeO}} \) are the molar fraction of PbO, Bi\(_2\)O\(_3\), B\(_2\)O\(_3\), FeO and \( d_{\text{PbO}}, d_{\text{Bi}_2\text{O}_3}, d_{\text{B}_2\text{O}_3}, d_{\text{FeO}} \) are the values of theoretical density of PbO, Bi\(_2\)O\(_3\), B\(_2\)O\(_3\), FeO, respectively [9]. The values of theoretical density for all the studied glasses are listed in Table 1. It is clear that, the values of density increase by increasing FeO content. The molecular weight of FeO (71.844 g/mol) is heavier than molecular weight of B\(_2\)O\(_3\) (69.62 g/mol) and hence, the glass matrix becomes more dense.

The molar volume

The molar volume \( (V_m) \) of the glass samples can be calculated from the following expression:

\[ V_m = \frac{M}{d} \]

Where \( M \) is the total molecular weight usually, the density of the glass changes in the inverse direction of the molar volume [5-7]. It was found that, the values of molar volume for all the studied samples which are listed in Table 1 decrease by increasing FeO content.

The theoretical optical electronegativity \( (\Delta \chi^*) \)

The theoretical optical electronegativity can be calculated [10] as follows:

\[ \Delta \chi^*_{\text{PbO}}, \Delta \chi^*_{\text{Bi}_2\text{O}_3}, \Delta \chi^*_{\text{B}_2\text{O}_3}, \Delta \chi^*_{\text{FeO}} \] are the values of theoretical optical electronegativity of PbO, Bi\(_2\)O\(_3\), B\(_2\)O\(_3\), FeO, respectively [10]. The values of optical electronegativity for all the studied samples are listed in Table 2.

The theoretical optical energy gap

The theoretical optical energy gap \( E_{\text{opt}} \) can be calculated [11]

\[ E_{\text{opt}} = \frac{\Delta \chi^*}{0.2668} \]

From Table 2, it is clear that, the value of theoretical optical band gap energy decreased by increasing FeO content. It was suggested [12] that the decrease in \( E_{\text{opt}} \) may be contributed by the \( E_{\text{opt}} \) of constituent oxides. If constituent oxides are considered to affect \( E_{\text{opt}} \) of the presently studied glass system, the replacement of B\(_2\)O\(_3\) \( (E_{\text{opt}}=69.62 \text{ eV}) \) with FeO \( (E_{\text{opt}}=71.844 \text{ eV}) \) contributes to the decrease in \( E_{\text{opt}} \) of the glass system. Also, it is clear that the theoretical values of \( E_{\text{opt}} \) are larger than the experimental values [8], this is due to amorphous nature of the prepared samples.

The theoretical optical basicity

The theoretical optical basicity\( (A_{\text{th}}) \) addresses the ability of oxide glass in contributing the negative charges in the glass matrix. In other words it defines the electron donating power of the oxygen in the oxide glass. The theoretical optical basicity can be calculated [11]

### TABLE 1. Composition, molecular weight, theoretical density, molar volume, for all the Studied samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Molecular weight (gm/mol)</th>
<th>Density (g/cm(^3)) (theoretical)</th>
<th>Molar volume (V(_m)) (cm(^3)/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>40PbO10Bi(_2)O(_3),49.8B(_2)O(_3),0.2FeO</td>
<td>170.690</td>
<td>5.291</td>
<td>32.260</td>
</tr>
<tr>
<td>40PbO10Bi(_2)O(_3),49.7B(_2)O(_3),0.3FeO</td>
<td>170.693</td>
<td>5.295</td>
<td>32.237</td>
</tr>
<tr>
<td>40PbO10Bi(_2)O(_3),49.6B(_2)O(_3),0.4FeO</td>
<td>170.695</td>
<td>5.298</td>
<td>32.219</td>
</tr>
<tr>
<td>40PbO10Bi(_2)O(_3),49.5B(_2)O(_3),0.5FeO</td>
<td>170.697</td>
<td>5.301</td>
<td>32.201</td>
</tr>
</tbody>
</table>

### TABLE 2. Composition, optical electronegativity, theoretical and experimental optical energy gap, for all the Studied samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Optical electronegativity</th>
<th>Theoretical optical energy gap (eV)</th>
<th>Experimental optical energy gap (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>40PbO10Bi(_2)O(_3),49.8B(_2)O(_3),0.2FeO</td>
<td>1.417</td>
<td>5.291</td>
<td>1.85</td>
</tr>
<tr>
<td>40PbO10Bi(_2)O(_3),49.7B(_2)O(_3),0.3FeO</td>
<td>1.415</td>
<td>5.264</td>
<td>1.73</td>
</tr>
<tr>
<td>40PbO10Bi(_2)O(_3),49.6B(_2)O(_3),0.4FeO</td>
<td>1.414</td>
<td>5.260</td>
<td>1.65</td>
</tr>
<tr>
<td>40PbO10Bi(_2)O(_3),49.5B(_2)O(_3),0.5FeO</td>
<td>1.412</td>
<td>5.253</td>
<td>1.60</td>
</tr>
</tbody>
</table>

TABLE 3. Composition, optical basicity, oxide ion polorazibility, refractive index, for all the Studied samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Optical basicity(A&lt;sub&gt;th&lt;/sub&gt;)</th>
<th>Oxide ion polorazibility(α&lt;sub&gt;02&lt;/sub&gt;)(Å&lt;sup&gt;3&lt;/sup&gt;)</th>
<th>Refractive index</th>
</tr>
</thead>
<tbody>
<tr>
<td>40PbO10Bi&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;49.8B&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;0.2FeO</td>
<td>0.9920</td>
<td>2.225</td>
<td>1.679</td>
</tr>
<tr>
<td>40PbO10Bi&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;49.7B&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;0.3FeO</td>
<td>0.9925</td>
<td>2.227</td>
<td>1.683</td>
</tr>
<tr>
<td>40PbO10Bi&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;49.6B&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;0.4FeO</td>
<td>0.9930</td>
<td>2.227</td>
<td>1.686</td>
</tr>
<tr>
<td>40PbO10Bi&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;49.5B&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;0.5FeO</td>
<td>0.9940</td>
<td>2.229</td>
<td>1.690</td>
</tr>
</tbody>
</table>

The values of theoretical optical basicity for all the studied samples are listed in Table [3]. The increased optical basicity of the glasses with FeO content indicates that the glass system is basic in nature.

The electronic polarizability of oxide ions (α<sub>02</sub>) can be calculated [11]

\[ \alpha(02) = -0.9 \chi_{sth} + 3.5 \]

It is clear that, the electronic polarizability of oxide ions increases with increasing the optical basicity. The values of electronic polarizability of oxide ions are listed in Table 3.

The linear refractive index

The linear refractive index, \( n_0 \), can be calculated [11]

The values of refractive index are listed in Table 3. The refractive index depends on the oxide ion polorazibility of glass material [13]. It is clear, that the values of the refractive index increase by increasing FeO content and increasing the values of oxide ion polorazibility.

The third order nonlinear susceptibility

The third order nonlinear susceptibility \( \chi^{(3)} \) (in esu units) is given by the following relation [5],

\[
\chi^{(3)} = \frac{1.4 \times 10^{-41} \left( E_{opt} - 1.96 \left( E_{opt} - 1.31 \left( E_{opt} - 0.65 \right) \right) \right)}
\]

The values of third order nonlinear susceptibility are listed in Table 4. It is clear that the high values of third order nonlinear optical susceptibility for all the studied samples are probably good candidates for nonlinear optical applications [14]. We have plotted the data of the of third order nonlinear susceptibility as a function of optical energy gap and refractive index of all the studied samples in Fig.1 and Fig. 2. It is seen that the third order nonlinear susceptibilities increase with decreasing the optical energy gap and increasing the refractive index for all the studied samples.

**Conclusion**

From all the above discussion, it was found that, the optical basicity of the glass materials increase by increasing number of oxide ion polarizability. The value of optical basicity shows that the glass materials are more basic. It is suggested that the ability of oxide ion to donate electrons to surrounding cations increases. Also, it was found that the values of third order nonlinear susceptibility increase with decreasing the optical energy gap and increasing the refractive index for all the studied samples. Finally, all the above values are a good basis for predicting new non linear optical materials.

TABLE 4. Composition, third order nonlinear susceptibility, for all the Studied samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>(Third order nonlinear susceptibility) ( \chi^{(3)} ) x10&lt;sup&gt;-14&lt;/sup&gt;esu</th>
</tr>
</thead>
<tbody>
<tr>
<td>40PbO10Bi&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;49.8B&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;0.2FeO</td>
<td>2.308</td>
</tr>
<tr>
<td>40PbO10Bi&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;49.7B&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;0.3FeO</td>
<td>2.323</td>
</tr>
<tr>
<td>40PbO10Bi&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;49.6B&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;0.4FeO</td>
<td>2.330</td>
</tr>
<tr>
<td>40PbO10Bi&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;49.5B&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;0.5FeO</td>
<td>2.342</td>
</tr>
</tbody>
</table>
Fig. 1. The third order nonlinear susceptibility as a function of optical energy gap

Fig. 2. The third order nonlinear susceptibility as a function of linear refractive index

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40\( \text{PbO} \) 10\( \text{Bi}_2\text{O}_3 \) (50-0.1)\( \text{B}_2\text{O}_3 \) \( x\text{FeO} \)

تم دراسة تأثير التغير الكيميائي على الخصائص الفيزيائية ل\( \text{PbO Bi}_2\text{O}_3\text{B}_2\text{O}_3 \) الهيدرات، وتم تشمل الخصائص الفيزيائية على الكثافة، الحجم المولاري، السالبية الكهربية، المنطقة المحرمة، معامل الاستقطاب الالكتروني، والثالث الثانوي غير الخطي.

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الخصائص الفيزيائية والضوئية لمركب الزجاج \( \text{PbO Bi}_2\text{O}_3\text{B}_2\text{O}_3 \) الداكن

غادة عادل وحنان مختار
قسم الفيزياء – كلية العلوم – جامعة الأزهر - مصر

40\( \text{PbO} \) 10\( \text{Bi}_2\text{O}_3 \) (50-0.1)\( \text{B}_2\text{O}_3 \) \( x\text{FeO} \)