Design a tunable glasses optical filters using CuO doped fluoroborate glasses

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\textbf{ABSTRACT}

Successfully, the glass composition (80\% B\textsubscript{2}O\textsubscript{3}−15\% NaF−5\%CaF\textsubscript{2}) was prepared using the melt quenching technique. Different CuO ratio from 0.3 wt\% up to 12 wt\% was added to the prepared glass composition at the expense of B\textsubscript{2}O\textsubscript{3}. The X-Ray diffraction pattern reveal the amorphous structure of the prepared glasses samples. The UV–Vis-NIR optical absorption spectrometer was used to investigate the optical properties of the glass samples. The structure was examined using the FTIR absorption spectroscopy. The optical absorption measurements reveal that the glasses sample from 0.30 wt\% up to 3.60 wt\% of CuO ratio produces band-pass glass filter samples. In addition, the CuO content of 6.0 wt\% and higher concentrations up to 12.0 wt\% give cut-off filters in the NIR region. The origin of the two types of filtering property was discussed in the frame of optical absorption and the changes in the glasses samples structure were discussed in the frame of FTIR absorption spectroscopy.

\section{1. Introduction}

During the last decades, great efforts have been done to fabricate optical filters covering different spectral ranges for large spectrum of optical applications. One of the most significant efforts are depositing layers of optical coatings onto a glass substrate which is one of the most common used methods to produce different kinds of optical filters [1]. Also, Flugh et al. introduced a rejection wavelength tunable optical filters based on Bragg diffraction [2,3]. In addition, low-loss fiber and narrowband laser transmitters developed based on Stimulated Brillouin Scattering reported by Cotter et al. [4]. More than that, electronically tunable acousto-optic filter based on CaMoO\textsubscript{4} relatively small birefringence was developed by Harris et al. [5]. Kaushik et al. [6] introduced an optical filter based on a sub-wavelength periodic structure for transmission of light through a resonant optical cavity by a dielectric layer. Other effort towards a wavelength tunable optical filter based on Fabry-Perot optical cavities interferometer was developed by Tawada et al. [7]. Finally, the melt-quenching technique was used by Kashif et al [8] using Lithium lead borate glass samples containing CuO to produce cut-off optical glasses filters. The same preparation methods was used to produce optical band pass filters in the visible spectral region [9]. Among all the methods used to produce optical filters, the melt-quenching technique is considered the most cost effective one. Phosphate glasses doped with CuO were also used as a host material for producing optical filters [10]. On the other hand, Borate glass doped with different alkaline was used as a host glass material by Lakshmi Narayana et al. [11] and, Okasha et al. [12], to produce optical filters. Borate glass has considerable low melting temperature. Adding other oxides like ZnO and NaO to the borate host glasses override its drawbacks like very low chemical durability and high affinity for water. On the other hand replacing the oxides with fluorides, which have low phonon energies compared with oxides, produce higher IR absorption edge than the host glass materials. This fluoride property allows to work as effective IR cut off window [13].

In the present study the fluoroborate glasses doped with CuO was prepared by melting quenching technique to produce different kinds of glass filters according to the CuO doped ratio. The present study also, is a part of our previous attempts to produce different kinds of optical filter using the same glasses composition with replacing CoO by CuO. [12].
2. Experimental work

2.1. Sample preparation

Samples of nominal composition (80% $B_2O_3$-15% NaF-5%CaF$_2$) were prepared from pure chemical reagents. Boric acid, $H_3BO_3$ (Laboratory Rasayan Sd Fine-Chem. Limited), sodium fluoride, NaF (Sisco research Lab. India), Calcium fluoride, CaF (Panreac Quimica SA, Espana and CuO (Sisco research Lab. India) were used as received without any further purification. The melt quenching technique was used to fabricate the glasses samples by mixing the weighted powder chemical in a large mortar, then added into a platinum crucibles and kept at 1200 $^\circ$C in an electric furnace for 2 h. the samples were swirled every half hour to insure the samples homogeneity. The samples casted in a stainless steel mold of proper shape and then transferred into a muffle furnace at 400 $^\circ$C and kept for 2 h for annealing. The muffle furnace switched off and allowed to cool overnight. The composition of ten named samples with different CuO content in addition to the base sample were illustrated in Table 1. The glasses samples stored in a glass desiccators after polishing with circular shapes of 1.5 cm radius and the thickness was adjusted to about 3 mm.

2.2. Characterization techniques

The XRD pattern was recorded using Philips Model PW3050/60 Diffractometer (40 KV, 30 mA) using Cu K$_\alpha$ radiation. The absorption and transmission spectra were carried out using UV–vis.-NIR Spectrophotometer (JASCO model V770) within the spectral range (200–1000 nm) for absorption and (200–2500) for transmittance. FTIR spectra were conducted using FTIR Spectrometer (Bruker Model Vertex 70) using the KBr disc technique within the spectral range 4000–400 cm$^{-1}$.

3. Results and discussion

3.1. X-Ray diffraction pattern

Fig. 1 shows the XRD pattern of the studied samples which indicates the amorphous structure of the samples and an evidence for the glass formation.

3.2. Optical absorption and transmittance

All the samples contain CuO showed green color which become darker with increasing the CuO. Fig. 2 shows a picture for the samples as prepared and without any treatments.

Fig. 3a illustrate the absorption spectra for the glasses samples containing CuO concentrations from 0.3% up to 6.0% giving band path filters.

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Fig. 3a illustrate the absorption spectra for the glasses samples containing CuO concentrations from 0.3% up to 6.0% in the range of 200 to 1000 nm. The strong absorption peak in the UV region attributed to the ferric ions traces may exist in row used chemical reagents [14]. By increasing the CuO content these absorption non-symmetric peaks become broader and red shifted from 370 nm up to 450 nm forming band pass optical filter property for the samples from 3 to 6% of CuO, respectively. The band pass filters become narrower and the symmetry increases. However, the height and the area under peak decrease by increasing the CuO up to 6.0% then the filter undergoes an opaque

<table>
<thead>
<tr>
<th>Sample name</th>
<th>$B_2O_3$ Wt%</th>
<th>NaF Wt%</th>
<th>CaF$_2$ Wt%</th>
<th>CuO Wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Base</td>
<td>80.00</td>
<td>15.00</td>
<td>5.00</td>
<td>0.00</td>
</tr>
<tr>
<td>Cu 0.3%</td>
<td>79.76</td>
<td>14.96</td>
<td>4.99</td>
<td>0.30</td>
</tr>
<tr>
<td>Cu 0.6%</td>
<td>79.52</td>
<td>14.91</td>
<td>4.97</td>
<td>0.60</td>
</tr>
<tr>
<td>Cu 1.2%</td>
<td>79.05</td>
<td>14.82</td>
<td>4.94</td>
<td>1.19</td>
</tr>
<tr>
<td>Cu 1.8%</td>
<td>78.59</td>
<td>14.73</td>
<td>4.91</td>
<td>1.77</td>
</tr>
<tr>
<td>Cu 3.0%</td>
<td>77.67</td>
<td>14.56</td>
<td>4.85</td>
<td>2.91</td>
</tr>
<tr>
<td>Cu 3.6%</td>
<td>77.22</td>
<td>14.48</td>
<td>4.83</td>
<td>3.47</td>
</tr>
<tr>
<td>Cu 3.6%</td>
<td>75.47</td>
<td>14.15</td>
<td>4.72</td>
<td>5.66</td>
</tr>
<tr>
<td>Cu 8%</td>
<td>74.07</td>
<td>13.89</td>
<td>4.63</td>
<td>7.41</td>
</tr>
<tr>
<td>Cu 10%</td>
<td>73.39</td>
<td>13.76</td>
<td>4.59</td>
<td>8.26</td>
</tr>
<tr>
<td>Cu 12%</td>
<td>72.73</td>
<td>13.64</td>
<td>4.55</td>
<td>9.09</td>
</tr>
</tbody>
</table>

Fig. 1. XRD pattern for the studied glass samples.

Fig. 2. A picture for as prepared samples.
3.3. Physical optical parameter

3.3.1. Band gap and refractive index

The optical band gap calculated from plotting \((a\nu)^{1/2}\) vs \((\nu)\), where \(a\) is the absorption coefficient, \(\nu\) is the photon energy. The energy gap value estimated from taking the intercept with extrapolation with zero absorption at x-axis. Fig. 6 shows the energy band gap for sample (Cu 0.3%) as a representative sample. The value of the band gap linearly decreases with the increase of the CuO content indicated indirect transition. The reason of the decrease of the band gap values may explain by increasing the conversion of the bridging oxygen to non-bridging oxygen states are 

\[
\frac{(n^2 - 1)}{(n^2 + 2)} = 1 - \sqrt{\frac{E_g}{20}}
\]

where \(E_g\) is the energy band gap of the studied glasses. The values of the optical band gap and the refractive index values are illustrated in Table 3.

The distribution of the refractive indexes with the wavelength are demonstrated in Fig. 5.

3.3.2. Density, molar volume molar refraction and electronic

Polarization

The density of the sample calculated according to the Archimedes principal using xylene as reference liquid solution from the equation:

\[
\rho = \frac{W_{air}}{W_{air} - W_l} \rho_{xylene}
\]

where \(W_{air}\) is the weight of the sample in air, \(W_l\) is the weight of the sample in xylene and \(\rho_{xylene}\) is the density of xylene.

The molar volume, \(V_m\), the molar refraction, \(R_m\), and the electronic polarization, \(\alpha_m\), may be calculated from the following equations [23]:

\[
V_m = M_m / \rho
\]

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

\[
\alpha_m = (3/(4\pi V_m)) R_m
\]

\[
\alpha_m = \alpha_{vis}/2.52
\]
Table 2
The peak height, FWHM, the full width, the center wavelength, cut-off and cut-on wavelengths for the studied samples.

<table>
<thead>
<tr>
<th>Filter type</th>
<th>(Cut-off) (nm)</th>
<th>(Cut-on) (nm)</th>
<th>(Center) (nm)</th>
<th>(Full Width) (nm)</th>
<th>(FWHM) (nm)</th>
<th>Peak height</th>
<th>sample</th>
</tr>
</thead>
<tbody>
<tr>
<td>Band-pass filter</td>
<td>792</td>
<td>314</td>
<td>501</td>
<td>195</td>
<td>229</td>
<td>75</td>
<td>Cu 0.3%</td>
</tr>
<tr>
<td>Band-pass filter</td>
<td>792</td>
<td>326</td>
<td>496</td>
<td>165</td>
<td>194</td>
<td>72</td>
<td>Cu 0.6%</td>
</tr>
<tr>
<td>Band-pass filter</td>
<td>792</td>
<td>329</td>
<td>499</td>
<td>164</td>
<td>194</td>
<td>55</td>
<td>Cu 1.2%</td>
</tr>
<tr>
<td>Band-pass filter</td>
<td>792</td>
<td>326</td>
<td>495</td>
<td>158</td>
<td>186</td>
<td>65</td>
<td>Cu 1.8%</td>
</tr>
<tr>
<td>Band-pass filter</td>
<td>740</td>
<td>350</td>
<td>508</td>
<td>120</td>
<td>141</td>
<td>41</td>
<td>Cu 3.0%</td>
</tr>
<tr>
<td>Band-pass filter</td>
<td>670</td>
<td>360</td>
<td>505</td>
<td>94</td>
<td>111</td>
<td>31</td>
<td>Cu 3.6%</td>
</tr>
<tr>
<td>Cut-off filter</td>
<td>1186</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>Cu 6.0%</td>
</tr>
<tr>
<td>Cut-off filter</td>
<td>1092</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>Cu 8.0%</td>
</tr>
<tr>
<td>Cut-off filter</td>
<td>1150</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>Cu 10%</td>
</tr>
<tr>
<td>Cut-off filter</td>
<td>1170</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>Cu 12%</td>
</tr>
</tbody>
</table>

Table 3
The band gab, $E_g$, the refractive index, $n$, the density, $\rho$, the molar volume, $V_m$, and the electronic polarization, $\alpha_m$, of the studied samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Band gab energy, $E_g$, (eV)</th>
<th>Refractive index $n$</th>
<th>Density $\rho$</th>
<th>Molar volume $V_m$</th>
<th>Molar refraction $R_m$</th>
<th>Electronic polarization $\alpha_m$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu 0.3%</td>
<td>3.33</td>
<td>1.52</td>
<td>1.82 ± 0.025</td>
<td>33.93704</td>
<td>10.31716</td>
<td>4.09412</td>
</tr>
<tr>
<td>Cu 0.6%</td>
<td>3.16</td>
<td>1.53</td>
<td>1.77 ± 0.025</td>
<td>34.86269</td>
<td>10.76905</td>
<td>4.27343</td>
</tr>
<tr>
<td>Cu 1.2%</td>
<td>3.09</td>
<td>1.54</td>
<td>1.75 ± 0.025</td>
<td>35.35997</td>
<td>11.65737</td>
<td>4.40249</td>
</tr>
<tr>
<td>Cu 1.8%</td>
<td>3.09</td>
<td>1.54</td>
<td>1.73 ± 0.025</td>
<td>35.87465</td>
<td>11.25576</td>
<td>4.46657</td>
</tr>
<tr>
<td>Cu 3.0%</td>
<td>2.70</td>
<td>1.57</td>
<td>1.65 ± 0.025</td>
<td>37.68762</td>
<td>12.36503</td>
<td>4.96976</td>
</tr>
<tr>
<td>Cu 3.6%</td>
<td>2.70</td>
<td>1.57</td>
<td>1.69 ± 0.025</td>
<td>36.80855</td>
<td>12.07661</td>
<td>4.79230</td>
</tr>
<tr>
<td>Cu 6.0%</td>
<td>2.43</td>
<td>1.60</td>
<td>1.65 ± 0.025</td>
<td>37.90592</td>
<td>12.96781</td>
<td>5.14598</td>
</tr>
<tr>
<td>Cu 8.0%</td>
<td>2.11</td>
<td>1.64</td>
<td>1.64 ± 0.025</td>
<td>38.26758</td>
<td>13.78730</td>
<td>5.47114</td>
</tr>
<tr>
<td>Cu 10%</td>
<td>2.10</td>
<td>1.63</td>
<td>1.66 ± 0.025</td>
<td>37.86347</td>
<td>13.64170</td>
<td>5.41337</td>
</tr>
<tr>
<td>Cu 12%</td>
<td>2.10</td>
<td>1.63</td>
<td>1.40 ± 0.025</td>
<td>45.12343</td>
<td>16.25737</td>
<td>6.45135</td>
</tr>
</tbody>
</table>

Fig. 5. The refractive index varying distribution with the wavelengths.

As a result of applying electric field on the sample the electronic polarization may varies and calculated using the Avogadro’s number, $N_A$, and the molar refraction, $R_m$. The Electronic polarizability can be related to the degree of electrons responses to an electric field calculated using both molar refraction and Avogadro’s number $N_A$. The obtained value of the calculated optical parameter are summarized in Table 3.

3.4 FTIR absorption spectral data

Fig. 7 shows the FTIR absorption spectra for selected sample covering the full range of the studied glass samples. In the base glass sample there were three prominent band observed. The first band from 400 cm$^{-1}$ to 1 to 750 cm$^{-1}$. In focus, this band include the peak at ~480 cm$^{-1}$ is reveal to the modified sites of the Na$^+$, Ca$^{2+}$ ions and/or Cu vibrations [12]. In addition, the peak at ~609 cm$^{-1}$ is caused by some borate groups which may exhibit deformation modes. The peak at ~690 cm$^{-1}$ is related to due to the bending vibration as the oxygen to B–O–B between one BO$_4$ unit and BO$_3$ [24]. The second broad band from 700 cm$^{-1}$ to 1200 cm$^{-1}$. The peak at ~930 cm$^{-1}$ is assigned to Vibration of BO$_4$ units. Appearing of the BO$_4$ group is an evidence for the similarity role of the CuO alkaline oxide on the transform ability of the BO$_3$ group to BO$_4$ group structure unit and supposed that the CuO is non-bridging Oxgen. The peak at ~1050 cm$^{-1}$ assigned to the stretching vibration of B-O in the tetrahedral structure of (BO$_4$F). The peak at ~1200 cm$^{-1}$ is related to the asymmetric stretching vibration of the triborate unit BO$_3$ [25]. The third broad band stating from 1200 cm$^{-1}$ to 1800 cm$^{-1}$. The peak at ~1350 cm$^{-1}$ is related to BO$_3$ units’ vibrations. The peak at ~1460 cm$^{-1}$ is related to –O$_2$BF vibrations. The absorption peak of triangular borate unit between 1200 cm and 1 to 1800 cm$^{-1}$ is larger than the tetrahedral borate one at 800 cm$^{-1}$ to 1200 cm$^{-1}$ and increase with adding CuO. This observation indicate that the conversion from triangular to tetrahedral increase with the increase of CuO as modifier.
In this work, we observed the influence of copper oxide (CuO) content on the optical properties of borate glasses. The FTIR spectra reveal the vibration modes of the glass matrix and the introduction of copper ions. The absorption peaks observed in the FTIR spectra are related to the vibrations of borate units and the stretching of Cu-O bonds. The absorbance bands at ~1000 cm⁻¹ are attributed to the bending vibrations of some borate units, which increase with the CuO content. The asymmetric stretching vibration of the triborate unit BO₃ is evident at ~1460 cm⁻¹, and the BOB linkage peak is observed at 700 cm⁻¹.

4. Conclusion

Increasing the CuO content in the glasses sample of composition (80% B₂O₃-15% NaF-5%CaF₂) produces glass samples with clear optical filter properties. Starting from 0.3% up to 6% of CuO content, the glass filters are band-pass filters. The centering wavelength, the band width, and the FWHM of the band-pass filter increase gradually by increasing the CuO content. While the height at the center wavelength decreases with increase the CuO content. From the point view of the optical absorption the origin of the optical property may explain by the splitting of “d” orbitals in the ligand field of the O₂ atoms in the lower wavelength and due to the existence of the Cu⁺ and Cu²⁺ ions in the higher wavelength. In the FTIR absorption spectra the BOB linkages peak at 700 cm⁻¹, the asymmetric stretching vibration of the triborate unit BO₃ at ~1460 cm⁻¹ and O₂BF vibrations peak at ~1460 cm⁻¹ exhibit increase in the intensity comparing with the base sample. This may related to the increase deformation modes of the bending vibrations of some borate units as a result of increasing the CuO content.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

References

