Preparation of Glasses containing Zn Ions by Sol-Gel Process

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Abstract: In this work were prepared glasses by using TEOS as precursor and Zn ions were added trough an aqueous solution before the gellification step. The preparation of this system is room temperature and the technique is very simple. These glasses were characterized by x-ray diffraction, optic absorption, FT-IR and Raman spectroscopy. The x-ray patterns show the typical amorphous features. The optical absorption shows a shoulder in the UV range corresponding with ZnO confined to the vitreous matrix. The spectra by FT-IR show characteristic vibrations of Si-O-Si with interaction Zn+2. The Raman scattering let us to identify the formation of the ZnO.

Key-Words: Glasses, Zn Ions and Sol-Gel Process.

1 Introduction

A very interesting use of the ZnO is like electronic devices with highly nonlinear current-voltage relationships (Varistors). At small applied electric fields, varistors are insulating; but at a fairly well-defined, higher field, they switch to conducting and maintain a nearly constant field over many decades of current. Most commercial, and military application varistors are based on polycrystalline, semiconducting ZnO with a variety of other oxide additives typically in the molar range of 100 parts per million to several percent. Their main application is in electrical circuits to limit or regulate the voltage that can be applied to other devices or components. While it is not unusual for all varistors to operate with current densities of $10^3$ to $10\text{ A/cm}^2$, some others applications also require unusually high electric fields near 40 kV/cm. With these high power conditions, it is perhaps not surprising those small flaws in the varistor result in breakdown, or a large irreversible change in their electrical and sometimes structural properties. The functional dependence of current on voltage in these devices is symmetrically bipolar that is due to an inherent property of the semiconductor from which it is made. The purpose of this work is to study an alternative way to prepare glasses containing Zn ions by using the sol-gel technique. The way to prepare this material is starting from TEOS as precursor and the Zn ions were added through an aqueous solution of Zn(CH$_3$COO)$_2$•2H$_2$O in the process, before the gel formation. The process is carry on at room temperature and the complete process is as simple as the sol-gel technique.

2 Materials and Methods

The samples with different compositions were prepared, where the ZnO molecules were embedded in the SiO$_2$ phase. The starting solutions were prepared by mixing tetraethyl orthosilicate (TEOS), water and ethanol. This set of samples was prepared using a constant ethanol:TEOS volume ratio of 1:1 and a volume ratio of water : TEOS volume ratio of 1:1. The solution was catalyzed with 50 drops of HCl in order to homogenize its phases (sol formation. After gelation, the all samples were dried and grounded.
to obtain a fine powder at room temperature. The zinc was incorporated into the samples, dissolving \( \text{Zn(CH}_3\text{COO)}_2 \) into water added to the starting solution. The amount of the zinc acetate varied from 0.1 M to 1.0 M, see Table 1.

<table>
<thead>
<tr>
<th>Sample</th>
<th>TEOS</th>
<th>PE</th>
<th>ZnAc Dihydrated</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10 ml</td>
<td>10 ml</td>
<td>10 ml, 0.1 M</td>
</tr>
<tr>
<td>2</td>
<td>10 ml</td>
<td>10 ml</td>
<td>10 ml, 0.2 M</td>
</tr>
<tr>
<td>3</td>
<td>10 ml</td>
<td>10 ml</td>
<td>10 ml, 0.3 M</td>
</tr>
<tr>
<td>4</td>
<td>10 ml</td>
<td>10 ml</td>
<td>10 ml, 0.4 M</td>
</tr>
<tr>
<td>5</td>
<td>10 ml</td>
<td>10 ml</td>
<td>10 ml, 0.5 M</td>
</tr>
<tr>
<td>6</td>
<td>10 ml</td>
<td>10 ml</td>
<td>10 ml, 0.6 M</td>
</tr>
<tr>
<td>7</td>
<td>10 ml</td>
<td>10 ml</td>
<td>10 ml, 0.7 M</td>
</tr>
<tr>
<td>8</td>
<td>10 ml</td>
<td>10 ml</td>
<td>10 ml, 0.8 M</td>
</tr>
<tr>
<td>9</td>
<td>10 ml</td>
<td>10 ml</td>
<td>10 ml, 0.9 M</td>
</tr>
<tr>
<td>10</td>
<td>10 ml</td>
<td>10 ml</td>
<td>10 ml, 1.0 M</td>
</tr>
</tbody>
</table>

A D8 Brucker Advanced equipment did the x-ray diffraction characterization, with a Cu source of 1.54 Å. The optical absorption was done in an S2000-UV-VIS Ocean Optics, Inc., and for the Raman spectroscopy was used a Raman Systems R-2000.

## 3 Results

The XRD patterns shown to us that all the samples were amorphous compounds, as can be seen in Figure 1, the behavior it is very similar between each gel. However we can see that the wide band between \( 2\theta = 17-35^\circ \) is better defined with increase of content acetate of zinc. A little peak appear at \( 2\theta=34^\circ \), wich can correspond to hexagonal ZnO structure.

Zinc oxide has a wide direct band gap of about 3 eV (400 nm). It is a great UV absorber. In Fig. 2 shows the absorption spectra with different contents of acetate of zinc. We can see an increasing of the optical absorption raising from 300 nm toward UV region in the graph. This plot also shows an absorption edge located at about 420 nm, (the inflection point), which means that ZnO is present in amorphous form in the samples. On other hand absorption spectra in the range 400-650 nm have behavioural similar between the samples, in general the absorption peaks are weaks in the zone of the 400-500 nm after this is constante.

In the Figure 3 is shown the IR spectrum of the majority of the studied samples. In order to understand the origin of the above glass structure in this spectrum is observed an intensive peak at 1100 cm\(^{-1}\), which can be attributed to characteristic vibration of Si-O-Si bridges in the silica network\(^1\). The band seen at 965 cm\(^{-1}\), can be related to the Si-O-H stretching vibration\(^3\), this peak with increased annealing temperature can disappears in the spectrum at 900 °C.

The band at around 800 cm\(^{-1}\) observed at low temperatute becomes much stronger at 900°C, very likely due to interaction between Zn\(^{+2}\) and the silica glass network which can result between the two characteristic bands for silica at 800 cm\(^{-1}\) and 470 cm\(^{-1}\).
Fig. 2 Absorption spectra of gels with acetate of zinc in the UV and VIS.

Fig. 3 Infrared spectrum of the gels with acetate of zinc.

From the Raman spectroscopy patterns it can be identified signals corresponding to ZnO, that can be seen in Figure 4.

Fig. 4. Raman spectra of gels with acetate of zinc.

The samples in pure powder form at RT show two Raman small signal at 435 cm\(^{-1}\) and 556 cm\(^{-1}\) corresponding to reported in other works\(^5\). Both peaks have a small intensity varying for different concentrations. The peaks at both positions are related with oxygen vacancies in ZnO\(^2\).

ZnO can be derived in Sol-Gel procedures starting with TEOS. In this case, Raman spectra will show a broad band raising from 500 to 550 cm\(^{-1}\).
corresponding to SiO$_2$. This band can overlap the second mentioned Raman signal for ZnO. The Fig. 4 shows Raman spectra for samples grown at room temperature, with different molar concentration. Two broad band are shown, corresponding to ZnO (435 cm$^{-1}$) and SiO$_2$, as we already appointed. As it can be seen, small molar concentrations result in larger peak intensities. The peak at 435 cm$^{-1}$ is related with E2 mode for ZnO. On other hand, Zinc acetate in pure form shows a large peak in its Raman Spectra, located at 960 cm$^{-1}$, as it can be see Fig. 5. This peak is related with CH-out of plane molecular stretching bond$^6$. In our samples, this peak disappears with the thermal treatment, due to breakage of the organic bonds by heating.

4 Conclusions

We obtained glasses containing ZnO, by the sol-gel technique. Starting from TEOS precursor, an SiO$_2$ solid matrix was obtained, containing ZnO in its pores. The glasses were amorphous, with stretching vibration of Zn-O and characteristic vibrations of Si-O-Si. The spectrum raman identified group ZnO and SiO$_2$.

References