Impact of bridging oxygens formation on optical properties of Fe$^{3+}$ doped Li$_2$O–Al$_2$O$_3$–SiO$_2$–TiO$_2$ glasses

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ABSTRACT

In this study, the structural chemistry of Fe$^{3+}$ doped Li$_2$O–Al$_2$O$_3$–SiO$_2$–TiO$_2$ (LAST) glasses has been analyzed utilizing UV-Vis spectroscopy. Optical parameters like absorption and extinction coefficients, indirect and direct optical band gaps, Urbach energy as well as Fermi energy level of samples were estimated via their absorption spectra. Then, it was tried to make a relationship between the variation of mentioned parameters and structural chemistry of different doped samples. Results of the investigation illustrated that even a little change in the microstructure of glassy samples has an effect on optical parameters and accordingly it could be sensible. Furthermore, it was revealed that Fe$^{3+}$ ions have the role of network forming in the structure of glass by increasing the formation of bridging oxygens (BOs) in the matrix.

KEYWORDS

UV-Vis absorption spectra, Glass, Short-range order, Bridging oxygens formation, Optical parameters, Structural chemistry

1. Introduction

Undoubtedly, progress in materials science will be limited due to the lack of data available on the microstructure of materials. Analysis of materials structure containing long-range order of crystals is a sort of a routine process. Nowadays there is a diversity of techniques which is being utilized for prediction of crystalline structures such as transmission electron microscopy (TEM), X-ray diffractometry (XRD) and so on [1–4]. Nevertheless, extraction of data is still in a serious doubt for the amorphous structures due to the short-range order of crystals distributed stochastically in the bulk of samples. In solid state chemistry, in order to investigate the structural evolution of amorphous materials, spectroscopic methods are used. Hence, various techniques have been proposed based on the interaction of electromagnetic wave (EW) with matter. Accordingly, interaction of EW in each region could be attributed to the resonance or absorption of EW by electrons, atoms, molecules, spin of electrons etc. Each of them could be interpreted for the structural evaluation [5–8].

In advanced technologies, heavy doped materials are utilized for production of the small, high power optical devices [9,10]. Glassy materials are the interested materials for production of small, high power devices due to their high solubility of dopants in amorphous matrix. It is almost obvious that introduction of a special dopant into a relatively suitable host could be used for the generation of precise optical and electrical devices. As a dopant, when d outer-shell electrons of transition metals is surrounded by the attraction and repulsion fields, there will be a special ligand field for the dopants which could lead to a special optical or electrical properties in the bulk [11–13]. According to the feather of LAS glasses like high transmissibility, near zero thermal expansion and non-linear optical properties, they are utilized in advanced applications. Due to the aforesaid characteristics, LAST glasses are recognized as precision optical apparatuses [14,15].

In this study, it is attempted to physically analyze the UV-Vis absorption spectrum of LAST glass doped by various amount of Fe$_2$O$_3$, then make a correlation between the physical parameters and structural chemistry of this matter.

2. Experimental procedure

Analytical reagents of Li$_2$CO$_3$, Al$_2$O$_3$, TiO$_2$, SiO$_2$ and Fe$_2$O$_3$ (Merck Company, Germany) were selected as the starting materials. Raw materials were thoroughly mixed to prepare about 50 gr batch. Then,
the mixed batch melted in alumina crucibles for 120 min at 1400 °C via conventional electrical furnace. The melted batch was poured into a pre-heated stainless steel mold and then allowed to cool down to the ambient temperature. Therefore, the composition of 14.5Li2O-19.8Al2O3-63.7SiO2-2TiO2 (wt%) doped with 0 to 1.5 wt% Fe2O3 was selected to prepare the glass specimens. ICP analysis (Wuxi Jiebo Electrical Technology Co., Ltd. China) was employed to calculate the solubility of alumina crucibles in the melt, and based on this data, the content of Al2O3 in the batch was justified.

3. Results and discussion

Adding transition metal oxides such as Fe2O3 to oxide glasses provides a new ability to enhance features of such materials to use in electronic, electrochemical, and electro-optic applications. Fe can appear as Fe2+ and Fe3+ in glassy matrix and lead to different developed structural units owing to the presence of various valence its states. Improvement of the chemical stability and durability of these glasses occurs by the addition of Fe2O3. Due to broad range of applications of transition metal ions and their influence in modification of the structure, it is very interesting to study in detail the effect of Fe2O3 addition on the structural, physical and optical properties of oxide glasses [16–18].

3.1. Spectra of UV-Vis absorption

Absorption spectra of LAST glasses containing 0-1.5% Fe2O3 dopant are shown in Fig. 1. Illustrated absorption edge in all glassy samples could be attributed to excitation of electrons in the samples. These graphs have been divided to three different regions. Each will be discussed in details in the following sections.

Fig. 1. UV-Vis absorption spectra related to LAST glass doped by different content of Fe2O3.

3.2. Calculation of absorption coefficient

In optics, a quantity characterizing how simply a medium or material can be penetrated via a light beam is known as the absorption coefficient [19]. The relative transparency of the medium to the light beam is recognized as a small absorption coefficient and the rapid absorption of a beam by a medium is known as the definition of a large absorption coefficient [20]. Units of reciprocal length are used to measure absorption coefficient.

\[
\alpha = \frac{1}{L} \ln \left( \frac{I_0}{I} \right)
\]

where \(\alpha\), \(L\), \(I_0\), and \(I\) are absorption coefficient, path length, the intensity of incident beam and intensity of transmitted beam, respectively [21]. It is explainable that optical constants of material, including absorption coefficient \(\alpha\) and refractive index \(n_o\), have effect on the electromagnetic waves spreading through sample in which \(n_o\) influences on their phase and \(\alpha\) affects the amplitude of beam waves. Absorption coefficient of samples was calculated for all range of UV-Vis spectra using Eq. 1.

3.3. Calculation of extinction coefficient

Imaginary section of the refraction complex index related to light absorption is recognized as extinction coefficient of sample that can be determined via Eq. 2:

\[
k = \alpha L / 4\pi
\]

where \(k\) and \(L\) shows extinction coefficient and the wavelength of EW in vacuum condition, respectively [11,22,23]. Using Eq. 2 extinction coefficient of each sample was calculated in whole UV-Vis range.

3.4. Direct and indirect band gaps

Based on Tauc’s reports [24,25], there is a relationship between absorption coefficient and band gap energy of a sample.

\[
\alpha(v) = \beta \left( \frac{hv - E_{gap}^0}{\epsilon_v^0} \right)^n / hv
\]

where \(E_{gap}^0\) shows the optical band gap of glass. \(h\) is the incident photon energy that has various values depending on the of incident light frequency that is probing the specimen. \(n\) that could be variable amounts 1/3, 1/2, 2, and 3, related to direct forbidden and direct allowed, indirect allowed, and indirect forbidden transitions, respectively. Plotting \((\alpha h\nu)^{1/n}\) versus photon energy \((h\nu)\) leads to drawing a direct line. In such cases, dividing intercept by slope equals to energy band gap of optical transitions [26]. \(\beta\) is a constant showing a temperature independent parameter called band tailing factor. It should be noted that this parameter depends on refractive index \(n_o\) of specimen calculated via:

\[
\beta = \sqrt{(4\pi / c)\sigma_o / n_o\Delta E}
\]

where \(\Delta E\) and \(\sigma_o\) are the tail width of localized states in the typically forbidden gap and the electrical conductivity at absolute zero [24,27]. Indirect and Direct optical band gaps of each sample are illustrated in Table 1.
3.5. Fermi energy level

Owing to weaker absorption of Visible photons than UV [28,29], extinction coefficient of various glass specimens can be obtained by Fermi-Dirac distribution function as

$$k(\lambda) = \frac{1}{1 + \exp((E_f - E_\lambda) / k_BT)}$$  \hspace{1cm} (5)

where $E_f$, $E$, and $k_BT$ are Fermi energy, the variable energy of sample probe photons and thermal energy resulting from ambient absolute temperature, respectively. $E_f$ can be obtained by fitting the least squares of Eq. 5. Fermi energy of different samples is illustrated in Table 1.

3.6. Urbach energy

Crystallinity degree of material is illustrated by proceeding of absorption coefficient with enhancement of incident beam energy right before absorption edge (3rd Tauc’s region). The adsorption coefficient gradually increases with a low slope up to the absorption edge for samples with disorder microstructure. The slope of this area increases as the degree of crystallinity rises. Eq. 6 can be used to calculate degree of crystallinity,

$$\alpha(v) = \beta \exp(hv / E_U)$$  \hspace{1cm} (6)

Where $E_U$ is the Urbach energy indicating the width of the band tail of localized states [20,26,29]. Table 1 displays the amount of Urbach energy for various Fe$^{3+}$ doped LAST glasses.

Changing of absorption coefficient with photon energy in many amorphous materials could be discussed in three different regions, according to Tauc [24],
- Exciton-phonon coupling region
- Interband transition (Tauc’s) region
- Urbach region

In the following, it will be tried to discuss more about each section and explain how their changes can be related to structural chemistry of amorphous specimens.

3.7. Exciton-phonon coupling region

The first region in UV-Vis absorption spectrum is recognized by almost constant absorption owing to exciton-phonon coupling. This mentioned area can be seen in the higher visible wavelengths. Fig. 2 shows the exciton-phonon region of spectra of UV-Vis absorption for LAST glass doped by different content of Fe$^{2+}$ dopant. As is obvious, absorption coefficient is more intensive for specimens containing higher amount of Fe$^{2+}$. In this case, exciton-phonon coupling increases by Fe$^{2+}$ enhancement. Exciton-phonon coupling will rises by increasing the differences between Fourier transform wave function of electrons and holes in a material. Although this effect is a general property of adding a dopant in a host, its intensive change shows that the selected dopant can change the electronic structure of LAST as well [30]. In the following section, these changes will be discussed in detail.

3.8. Interband transition (Tauc’s) region

The second part of UV-Vis absorption spectrum recognized as Tauc region. This region is related to high absorption, which can be employed to calculate optical band gap and is associated with interband transitions. The Tauc’s region of LAST glasses doped with different Fe$^{2+}$ content is shown Fig. 3.

As it is illustrated, absorption edge shifts toward larger wavelengths of electromagnetic wave by increasing the amount of Fe$^{2+}$ in samples. Accordingly, reduction of band gap and Fermi energy level will be predictable for heavy-doped samples.

In the electronic band structure graphs of materials, the difference of energy (in electron volts) between the bottom of the conduction band and the top of the valence band in insulators and semiconductors generally narrates the band gap. This band equals to the energy needed to free one electron from the outer shell of its orbit around the nucleus to change to a carrier of the movable charge, and to move freely in the solid. Therefore, an important determinant parameter of electrical conductivity of the material is the band gap. There are several ways to transfer the electrons in solid between energy levels [31]. The electron transition from the bottom valence band to top conduction band stimulated in frequency of absorption edge is the highest energy transition that can be determined by Eq. 7:

$$E_g = \frac{hc}{\lambda_{ae}}$$  \hspace{1cm} (7)

where $E_g$, $h$, $c$, and $\lambda_{ae}$ are the band gap energy, the plank’s constant, the speed of light propagating in vacuum, and the wavelength of absorption edge, respectively [26].

| Sample        | $E_f$ | Direct band gap | Indirect band gap | $E_U$ |
|---------------|-------|----------------|-------------------|-------|
| 0% Fe$^{2+}$  | 3.94  | 2.77           | 3.51              | 0.41  |
| 0.5% Fe$^{2+}$| 3.66  | 2.53           | 3.22              | 0.32  |
| 1% Fe$^{2+}$  | 3.27  | 2.46           | 2.92              | 0.28  |
| 1.5% Fe$^{2+}$| 3.16  | 2.33           | 2.56              | 0.24  |

Table 1. Energy states of Fe$^{2+}$-doped LAST glass.

Fig. 2 Exciton-phonon coupling region of spectra of UV-Vis absorption for LAST glass doped by different content of Fe$^{2+}$.
According to Table 1, increasing the content of dopant leads to a decrease in indirect and direct optical band gaps. Obviously, introduction of Fe$^{3+}$ ions in the glassy matrix has led to the broadening of conduction band. Al$^{3+}$ ions replace by Fe$^{3+}$ ions. Due to the different ligand field around these ions compared to the other positive ions e.g. Si$^{4+}$, Al$^{3+}$ and Ti$^{4+}$, some bands form close to the conduction band. These bands are so close together and the collection of them forms a wide band broadened into the band gap. Hence, band gaps will be reduced. The intensive reduction of indirect band gap of samples by increasing the Fe$_2$O$_3$ content (from 3.51 to 3.56) shows the ability of Fe$^{3+}$ ions for giving semiconducting effect to parent glass [32–35].

According to Tauc [24], the decrease in Fermi energy level by enhancement of the Fe$_2$O$_3$ content can be attributed to the increase in ionic bonds in the matrix. Compared to the covalent bonds, ionic bonds are increased by introduction of Fe$^{3+}$ ions; hence, Fermi level is fallen to lower energy levels.

### 3.9. Urbach region

An exponential region in UV-Vis absorption spectrum (The 3rd region) is called Urbach region. This region that lies between Tauc’s and exciton-phonon regions is shown for different Fe$_2$O$_3$ doped LAST glasses in Fig. 4.

It is reported that many parameters such as electric fields of defects, thermal vibrations, dislocations, and etc. can create tailing of energy states in the forbidden energy gap [36,37]. Exciton-phonon coupling (dynamic disorder) is the significant item that contributes to edge broadening in crystalline materials. In amorphous ones, existing static disordering results in an additional broadening. Hence, the Urbach energy is resolved in two parts:

$$ E_u = E_d + E_{ph} $$

where, $E_d$ and $E_{ph}$ are related to phonon and disorder-induced broadening. $E_d$ is considered temperature-independent, while $E_{ph}$ depends on temperature according to following relation [38,39]:

$$ E_{ph} = A \coth \left( \frac{B}{2kT} \right) $$

where, $A$ and $B$ are constants that are not temperature dependent.

Based on Eq. 8, the zero-level vibrations result in remaining of a non-zero dynamic disorder remains even at low temperatures, but it is almost constant for various doped glassy materials. Therefore, change in Urbach energy significantly can be owing to disorder-induced broadening. Considering the results determined from $\ln(\alpha)$-$h\nu$ diagrams, increasing the amount of Fe$_2$O$_3$ in the sample leads to a decrease in Urbach energy. It means that microstructure of samples will be more ordered by introduction of Fe$^{3+}$ ions in the glassy matrix of LAST. According to reports, this change could be attributed to formation of bridging oxygens (BOs) in the matrix. Tetrahedral chains of SiO$_4^{4+}$ are joined together using O-linkers and the matrix goes toward the crystalline materials [14,40].

### 4. Conclusions

Structural chemistry of LAST glass in presence of Fe$^{3+}$ ions was evaluated using the investigation of optical properties of samples calculated from their UV-Vis absorption spectra. Hence, reducing the Urbach energy, Fermi energy level and optical band gaps by enhancement the Fe$_2$O$_3$ content in the specimens was ascribed to the...
broadening of conduction band owing to the formation of new bands close to the conduction band, increasing ionic bonds in the matrix and formation of more ordered structure owing to the formation of bridging oxygens.

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