Optical Properties of TeO_2 SrO B_2O_3 V_2O_5 Glass System

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The physical and optical properties of glasses having a composition $59TeO_2$ x SrO (40-x) B_2O_3 $1V_2O_5$, where (x = 10, 20, 30) have been studied. It was found that the values of density and molar volume increase by increasing SrO content for all the studied samples. Also, it was found that the values of the optical energy gap decrease while as the values of the refractive index increase by increasing SrO content. The optical basicity of the glasses and the polarizability of oxide ions have been calculated. It has been found that all the studied glasses become more polarized and more basic by increasing SrO content. Also, all the studied samples show insulating behavior. Finally, all the prepared samples have higher values of third order nonlinear susceptibility (6.92-8.34) $x10^{-13}$ esu, this means that all the studied samples are promising materials for nonlinear optical devices.

1. Introduction

The materials of high optical nonlinearity become of interest in science and technology of materials after the discovery of the laser in 1962. The primary focus was on the second and third order optical nonlinearity. In particular, the third order nonlinear optical materials have attract much attention because of their great importance in the field of optical, computing and information technology, as they have possible application in photonic devices for frequency generation, modulation, and optical memory. Dimitrov and Sakka [1], suggested that oxides which have a narrow optical energy gap and a high nonlinear refractive index are found to have a metallization criterion of nearly (0.30-0.45). Oxides with a high nonlinear refractive index are found [2, 3] to have high values of optical basicity and high values of oxide ion polarizability. Telluride glasses have high optical nonlinearity and have practical application as nonlinear optical materials [4]. The structural, optical and electrical properties of these glasses have been studied [5-8]. Borate glasses have been attracted attention due to their practical applications in the fields of linear and nonlinear optics and correlated techniques [9]. $SrOB_2O_3$ glasses have good value in mass attenuation coefficient and effective atomic number which make them good radiation shielding materials [10]. The optical

properties of Bi_2O_3 SrO B_2O_3 glasses have been studied [11]. It has been found that these glasses have narrow optical energy gap and high refractive index. The aim of the present work is to study the optical and the physical properties of $59TeO_2$ x SrO (40-x) B_2O_3 $1V_2O_5$ glasses, where (x = 10, 20, 30).

2. Experimental

Glasses having a composition $59TeO_2$ xSrO (40-x) B_2O_3 $1V_2O_5$, where (x = 10, 20, 30) were prepared by the conventional melt quench technique. Proper weights of TeO_2, SrO, B_2O_3, V_2O_5 in accurate molar ratio were mixed to obtain uniform acceptable fine powder and then, placed in a porcelain crucible and heated in an electric furnace whose temperature was elevated in steps to 1100^0C for half an hour. Then, the molten samples were rapidly cooled to room temperature by pouring it onto a cooper plate and successively pressing it with another to gain glasses. The studied samples have been characterized by the X-ray diffraction (XRD). All the samples reveal non-crystalline nature as no noticeable peaks were detected in (XRD) spectra. The absorption of all the samples in the wave length (400-800nm) was measured using a computerized recording spectrophotometer (type Jasco, V-570).

3. Results and Discussions

3.1. The Density

The glass density was determined by Archimedes method .The values of density for all the studied samples are listed in table (1).

Table (1): "The values of density, molecular weight, molar volume and oxygen packing density for all the studied samples":

sample	Density (g/cm^3)	Molar volume (cm^3/mol)	Molecular weight (g/mol)	Oxygen packing density
$59TeO_2 10SrO 30B_2O_3 1V_2O_5$	4.42	27.21	120.27	81.95
$59TeO_2 20SrO 20B_2O_3 1V_2O_5$	4.72	27.68	130.63	73.35
$59TeO_2 30SrO 10B_2O_3 1V_2O_5$	4.80	27.92	134.03	66.90

The molar volume V_m can be calculated as following,

The molar volume = (Total molecular weight)/(density) …… (1)

The values of molar volume for all the studied samples are listed in Table (1). It is clear that the density increases because the molecular weight increases by increasing SrO content for all samples. Generally, the density and the molar volume show opposite behaviors. It was found that the molar volume increases

for all samples. The increase of the molar volume can be resulted from an increase in the bond length or an increase in the interatomic space between atoms.Oxygen packing density is the arrangement of the oxygen atoms in the glass system and can be calculated as follows,

$$\text{Oxygen packing density} = (1000\text{xO})/ V_m \quad \text{……………. (2)}$$

Where, O denotes the sum of oxygen in the oxide glass system. The reduction in the oxygen packing density is most likely due to the decrease in number of oxygen atoms in the molecule.

3.2. The Optical Basicity:

The high optical basicity means high electron donating power of the oxygen in the oxide glass. The optical basicity can be calculated [1] as follows,

$$\text{Optical basicity}=x(TeO_2)\Lambda(TeO_2)+ x(SrO)\ \Lambda(SrO)+ x(B_2O_3)\ \Lambda\ (B_2O_3) + x(V_2O_5)\ \Lambda\ (V_2O_5) \quad \text{………………………….. (3)}$$

Where x (TeO_2), x (SrO), x (B_2O_3) and x (TeO_2) are the corresponding portion of the different oxides. And **Λ** (TeO_2), **Λ** (SrO), **Λ** (B_2O_3) and **Λ** (V_2O_5), are the optical basicity values of the principal oxides. It is clear from table (2), that the values of optical basicity increase by increasing SrO content, which means that the studied glasses become more basic.

3.3. Polarizability of Oxide Ions:

The relation between electronic polarizability of oxide ions and optical basicity of oxide is calculated as follows [1],

$$\text{polarizability of oxide ion} =1.67/(1.67\text{-optical basicity}) \quad \text{……………. (4)}$$

From table (2), it was found that, by increasing SrO, the values of the electronic polarizability of oxide ions increase. This means that the glasses become more polarized.

Table (2): "The values of optical basicity, polarizability of oxide ions for all the studied samples":

Sample	optical basicity	polarizability of oxide ions
$59TeO_210SrO30B_2O_31V_2O_5$	0.821	1.967
$59TeO_220SrO20B_2O_31V_2O_5$	0.897	2.160
$59TeO_230SrO10B_2O_31V_2O_5$	0.973	2.396

3.4. Differential Scanning Calorimeter (DSC) Analysis:

Typical DSC traces of $59TeO_2$ xSrO (40-x) B_2O_3 $1V_2O_5$ powder glasses recorded at heating rate 10 deg./min. are shown in Fig.(1). Table (3), represents the values of the glass transition temperature, T_g, the crystallization temperature T_p, and the melting temperature T_m for all the samples under study. From the table, it was found that the transition temperatures (T_g,T_p,T_m) decrease by increasing SrO content. The difference ($\Delta T=T_p-T_g$) increases by increasing SrO content as shown in Table (3) so that ,the thermal stability increases by increasing SrO content. This is in fair agreement with the above arguments. The density increase by increasing SrO content i.e, the bond strength increases, this along with the polarizability data suggest the increase of thermal stability.

Table (3): "Transition temperatures and thermal stability for all the studied samples":

Sample	$T_g(^0C)$	$T_p(^0C)$	$T_m(^0C)$	ΔT
$59TeO_2 10SrO 30B_2O_3 1V_2O_5$	468.3	543.3	771.2	75
$59TeO_2 20SrO 20B_2O_3 1V_2O_5$	430.2	508.2	765.0	78
$59TeO_2 30SrO 10B_2O_3 1V_2O_5$	390.8	469.8	759.8	79

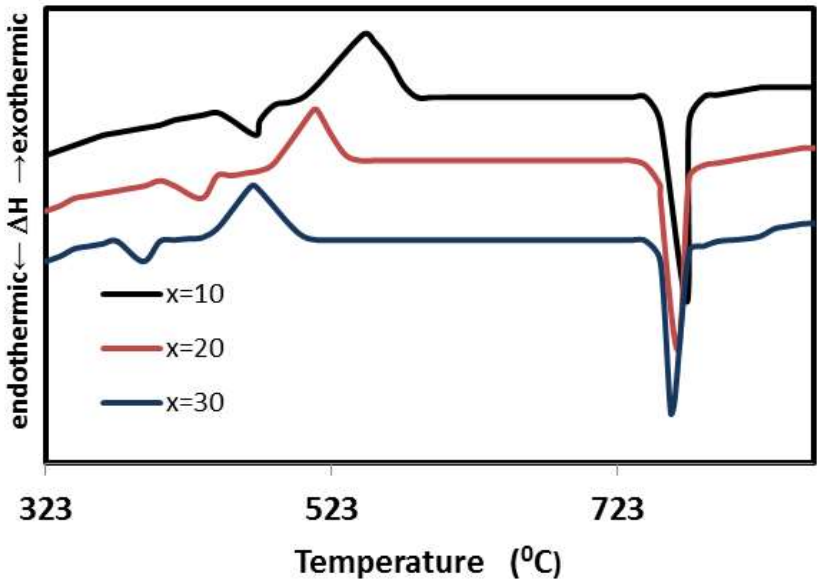
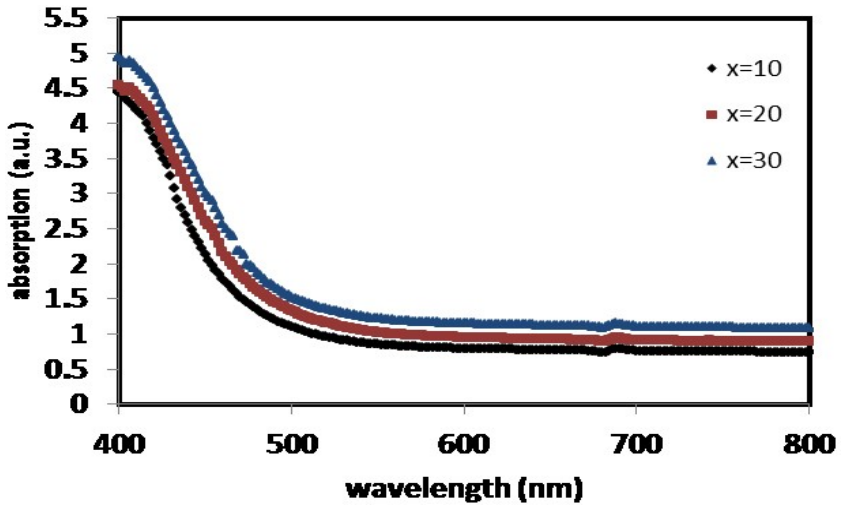


Figure (1): DSC spectra for all the studied samples.

3.5. Optical Energy Gap:

Figure (2) shows the optical absorbance spectra for all the studied samples. The absorption coefficient α of each sample was calculated using the relation[12].

$$\alpha= (2.303xA)/ t \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (5)$$



Figure(2): The optical absorbance spectra for all the studied samples.

Where A is the absorbance and t is the thickness of the sample. Mott and Davis [12] proposed the relation between the absorption coefficient α(ω) and the photon energy ħω of the incident radiation, this relation can be written as follows,

$$\alpha\hbar\omega=\beta(\hbar\omega-E_{opt})^{n} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (6)$$

Where ω is the angular frequency of radiation, β is constant called band parameter, E_{opt} is the optical energy gap and n is a parameter that characterizes the transition process (n=1/2 for a direct allowed transition, n=3/2 for direct forbidden transition, n=2 for indirect allowed transition and n=3 for direct forbidden transition). Plots of $(\alpha\hbar\omega)^{1/2}$, $(\alpha\hbar\omega)^{2}$, $(\alpha\hbar\omega)^{2/3}$ and $(\alpha\hbar\omega)^{1/3}$ versus the photon energy are obtained. Extrapolation of the linear part to the x-axis is well fitted over a wide energy range by n=2. The proposed absorption mechanism is indirect one. This is expected due to the lack of translate symmetry, where the wave vector is not good quantum number. The values of E_{opt} corresponding to the energy separation between extended states in the valence and conduction band are defined as the intersection between $(\alpha\hbar\omega)^{1/2}$ and ħω as shown in Fig. (3).

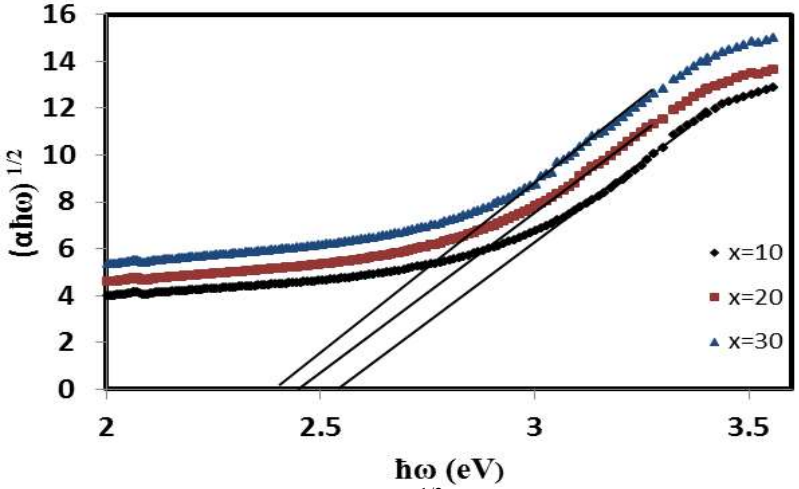


Figure (3): The relation between $(\alpha\hbar\omega)^{1/2}$ and ħω for all the studied samples.

The obtained values of E_{opt} for all the studied glasses are given in Table [4]. It is clear that, the value of optical band gap energy decrease by increasing SrO content. As a result of the replacement of $B_2O_3$with SrO, the structural changes take place inside the glass. As SrO in the glass matrix increases, B-O-Te is replaced with Sr-O-Te. These structural changes will result in shifting the valence band maximum to higher energies, thus reducing the band gap of the glass system,

Table (4): "The values of optical energy gap, refractive index, third order nonlinear susceptibility and metallization for all the studied samples":

sample	optical energy gap (eV)	refractive index	third order nonlinear susceptibility (e.s.u)	Metallization
$59TeO_2 10SrO 30B_2O_3 1V_2O_5$	2.55	2.15	$6.92x10^{-13}$	0.357
$59TeO_2 20SrO 20B_2O_3 1V_2O_5$	2.45	2.17	$7.60x10^{-13}$	0.350
$59TeO_2 30SrO 10B_2O_3 1V_2O_5$	2.40	2.19	$8.34x10^{-13}$	0.346

3.6. The Linear Refractive Index:

The calculation of the refractive index is very important to know the suitability of glass material to be optical devices[13].The refractive index, n, can be calculated from the value of E_{opt} using the formula proposed by Dimitro and Sakka [14] as follows:

$$(n^2-1)/(n^2+1)=1-(E_{opt}/20)^{1/2} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (7)$$

The values of refractive index for all the studied samples are listed in Table (4). It is clear, that by increasing SrO content, the values of the refractive index increase. The values of refractive index increase because the values of the polarizability of oxide ions increase by increasing SrO content for all samples.

3.7 Third order nonlinear susceptibility:

The high polarizability of oxide ions accounts to the noticed nonlinear optical properties of the glasses. The glasses with higher nonlinear optical properties, especially third order nonlinear susceptibility, are desirable to develop nonlinear waveguide devices applicable to optical signal processing [1]. The third order nonlinear susceptibility in esu units was calculated from the values of the refractive index by the following relation [15],

$$\chi^{(3)} = ((n^2-1)/ 4\pi)^4 \times 10^{-10} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (8)$$

It was found that the values of third order nonlinear susceptibility which are listed in table (4) are higher than that of pure silica glass ($2.8x10^{-14}$ e.s.u), which means that all the studied samples are promising materials for nonlinear optical devices. Also, It was noticed that the values of third order nonlinear optical susceptibility increase by increasing SrO content as a result of increasing the values of refractive index for all the studied samples.

3.8. Metallization criterion of the glasses:

Dimitrov and Sakka [1] calculated metallization criterion for various simple oxides and found that oxides with large refractive index and small energy gap have small metallization criterion .

$$\textbf{The metallization criterion} = [E_{opt}/20]^{0.5} \quad \ldots\ldots\ldots\ldots (9)$$

The values of metallization criterion for all the studied samples are listed in Table (4). It was found that the metallization criterion values of the present glasses are found to be less than one and thus all the studied samples exhibit insulating behavior [1] .Also, it was found that the values of metallization decrease by increasing SrO because the values of optical energy gap decrease for all the studied samples.

Conclusion:

From all the above arguments, it was found that the values of density, molar volume, refractive index, increase by increasing SrO content. On the other hand, the values optical energy gap, decrease by increasing SrO content. Also all the studied samples exhibit insulating behavior and become more basic and more polarized by increasing SrO content. The high values of third order nonlinear optical susceptibility for all the studied samples were found to be in the range (6.92-8.34) x 10^{-13}esu. Finally, all the studied samples are promising materials for nonlinear optical devices.

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