Egypt. J. Phys. **Vol. 46,** pp. 23 - 28 (2018)

Physical Properties of Nb_2O_5BaO TeO_2 Glass System with Compositional Variations

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THE INFLUENCE of compositional variations on the physical properties such as, density, molar volume, ,molar refraction, optical energy gap, refractive index , optical basicity, oxide ion polarizability, metallization, and third order nonlinear susceptibility, nonlinear refractive index, with the variation in Nb_2O_5 content has been studied theoretically for glasses of compositions $xNb_2O_5(20-x)BaO80TeO_2$ (x=0, 5, 10,15) and the physical parameters related to these compositions were analyzed with theoretical predictions.The density calculated decreases with the increase of Nb_2O_5 content from 5.680 g cm^{-3} to 5.493 g cm^{-3}, this means that the glass matrix becomes less dense. It was found that , the optical energy gap decreases, but the refractive index increases by increasing Nb_2O_5 content.The electronic polarizability of oxide ion decreases with decreasing the optical basicity. The value of optical basicity shows that the glass materials are less basic. It is suggested that by increasing Nb_2O_5 content ,the glasses become less polarized. Also, It was found that the values of third order nonlinear susceptibility increases by increasing Nb_2O_5 content and are found to be larger than those of the silica based glasses. The glasses are found to possess a high refractive index (2.170–2.213), a comparatively narrow band gap (3.992eV–3.785eV), high electronic ion polarizability (2.445 $Å^3$-2.546 $Å^3$) and high optical basicity (0.987–1.014). It was found that the values of the third order nonlinear optical susceptibility are in the range (0.7604-0.9271)x10^{-12}esu. Finally, all the above values are a good basis for predicting new non linear optical materials.

Introduction

Due to technological importance of nonlinear optical materials,the nature of the nonlinear optical phenomena has been studied to predict a new nonlinear optical properties.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 [1]. It has been established that the nonlinear refractive index increases with increasing linear refractive index and decreasing energy gap of the oxides. This is related to the increasing metallicity of the oxides. Oxides with a high nonlinear refractive index posses a metallization criterion of approximately (0.30–0.45).The optical basicity has been proved also to be a useful parameter for correlating and predicting properties of oxide systems covering a broad range of application [2]. The theoretical optical basicity, 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 [2].Electronic polarizability of ions demonstrates the easy of deformation of their electronic clouds by applying of an electromagnetic field. It is closely related to many properties of the materials such as refraction, conductivity, ferroelectricity, electro-optical effect, optical basicity along with optical nonlinearity [3,4]. That is why today's knowledge of the state of polarization of ions in different crystallineand amorphous materials is of significant interest. The estimation of the electronic polarizability of ions is subject of the so-called polarizability approach in materials science, which is well known especially in the field of glass science as done by Weyl and Marboe [5]. Recently, the polarizability approach has been systematically developed in our recent papers concerning the origin of electronic polarizability and optical basicity of simple oxides [6] and oxide glasses [7,8]. The polarizabilityapproach has shown renewed interest because of the need to design optical functional materials and to search for novel glasses with higher optical performances such as oxide glasses with high second- and third order optical nonlinearities [7,8]. Tellurite glasses have been become

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DOI : 10.21608/ejphysics.2018.3668.1003

interesting materials for structural, optical and electrical investigations [9-11] due to their high third order optical nonlinear susceptibility. For pure TeO_2 glass ,it was found [12] that the value of third order optical nonlinear susceptibility equals ($1.4x10^{-12}$esu), however,it is not easy to obtain this pure glass.The xNb_2O_5-20BaO-80TeO_2 glass samples with x= 0,5,10 and 15 mol % have been prepared [13] using the conventional solid state method and melt-quenching technique. Powders of Nb2O5, BaO and TeO2 with purity >99.95%-99.99% was mixed and ground in an agate mortar in an hour to reach good homogeneity and fined grained mixture. The mixed batches were then melted for an hour at 900°C .Then, the melt was quenched to room temperature by pouring it on a stainless steel plate and subsequently pressing it with another to obtain glasses.Optical absorption spectra were recorded using Varian Cany 5000 UV-VIS-NIR spectrometer with wavelength range between 200-1000 nm at room temperature. It was suggested[13] that the decrease in optical energy gap may not be related to structural change but contributed by the optical energy gap of constituent oxides. If constituent oxides is considered to affect optical energy gap of the presently studied glass system, the replacement of BaO (E_{opt}=4.80eV) with Nb_2O_5(E_{opt}=3.40 eV[6] contributes to the decrease in E_{opt}.of the glass system.The aim of the present work is to calculate theoretically thephysical properties of x Nb_2O_5 (20-x) BaO 80TeO_2glasses where (x = 0,5,10,15) and compare it with the experimental results[13].

Theoretical calculations

The density (d) of all the glasses under study can be calculated from the following expression:

$$d=(x_{Nb2O5}\, b_{Nb2O5}+x_{BaO}\, d_{BaO}+x_{TeO2}\, d_{TeO2}) \quad (1)$$

where, xis the molar fraction and d is the value of theoretical density ,respectively[6].

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

$$V_m = \frac{M}{d} \quad (2)$$

where M is the total molecular weight

The theoretical optical energy gap values have been calculated using Shimakawa's relation as [14],

$$E_{opt}= x_{Nb2O5}E_{opt}(Nb_2O_5)+xBaOE_{opt}(BaO)+x_{TeO2}E_{opt}(TeO_2) \quad (3)$$

where xis the molar fraction.and E_{opt} is the value of theoretical optical energy gap, respectively [6].

The theoretical optical basicity(A_{th}) can be calculated according to the approach proposed by Duffy and Ingram [15].

$$A_{th}=X(Nb_2O_5)A(Nb_2O_5)+X(BaO)A(BaO)+X(TeO_2)A(TeO_2) \quad (4)$$

where x is the equivalent fraction of the different oxides, i.e. the proportion of the oxide atom that contributes to the glass system; A is the optical basicity values of the constituent oxides [6].

The relationship between electronic polarizability (α^{02-}) of oxide ions and optical basicity of oxide is given by this equation [16]

$$\alpha^{02-} = \frac{(1.67)}{(1.67-A_{th})} \quad (5)$$

The molar refraction (R_m) can be calculated [16] with respect to the optical band gap.

$$R_m = V_m\left(1-\sqrt{\left(\frac{E_{opt}}{20}\right)}\right) \quad (6)$$

The calculation of the refractive index is very important to determine the suitability of glass material to be optical devices[17].The refractive index, n_0, can be calculated from the value of E_{opt} using the formula proposed by Dimitro and Sakka [16] as follows :

$$n_o = \sqrt{\left(\frac{(V_m+2R_m)}{(V_m-R_m)}\right)} \quad (7)$$

The metallization criterion(M_c) (the nature of metallic and non metallic of oxide glasses) can be calculated and explained [16] on predicting the nature of solids which is metallic or non metallic based on the condition of (molar refraction /molar volume)<1(insulator) and >1(metal) ,by using the following equation [16],

$$M_c = 1-\left(\frac{R_m}{V_m}\right) \quad (8)$$

The glasses with higher nonlinear optical properties, especially third order nonlinear susceptibility are desirable to develop nonlinear waveguide devices applicable to optical signal processing [18]. The third order nonlinear susceptibility$\chi^{(3)}$ in esu

units is given by the following relation [19]:

$$\chi^{(3)} = \left(\frac{(n_o)^2-1}{4\pi}\right)^4 x10^{-10} \quad (9)$$

Results and Discussion

Density and molar volume

The values of density for all the studied glasses are listed in Table 1. It is clear that, the values of density decrease by increasingNb_2O_5 content. It was suggested [13] that the decrease in density may be contributed by the densityof constituent oxides. If constituent oxides is considered to affect density of the presently studied glass system, the replacement of BaO (E_{opt}=5.72 g/cm3) with Nb_2O_5 (density=2.46 g/cm3) [6] contributes to the decrease in density of the glass system.The values of molar volume changes in the inverse direction of the density ,as listed in Table 1.

Theoreticaloptical energy gap

The values of theoretical optical energy gap are listed in Table 2. It is clear that the values of optical energy gap decrease by increasing Nb_2O_5 content.It was suggested [13] that the decrease in E_{opt} may be contributed by the $E_{opt}$of constituent oxides. If constituent oxides is considered to affect E_{opt} of the presently studied glass system, the replacement ofNb_2O_5(E_{opt}=3.40 eV)with BaO (E_{opt}=4.80eV)[6] contributes to the decrease in E_{opt}.of the glass system.Also, it was found that the values of theoretical optical energy gap are larger than experimental one [13] due to the amorphous nature of prepared glasses.

The theoretical optical basicity

It is clear from Table 3, that the values of optical basicity decrease by increasing Nb_2O_5content.It was suggested [16] that the decrease in optical basicity may be contributed by the optical basicityof constituent oxides. If constituent oxides is considered to affect optical basicity of the presently studied glass system, the replacement of BaO (A=1.23) with Nb_2O_5 (A=1.05) [6] contributes to the decrease in optical basicity of the glass system.

Oxide ion polarizability

From Table 3, it is clear that, by increasing Nb_2O_5, the values of the electronic polarizability of oxide ions decrease. This means that by increasing Nb_2O_5content ,the glasses become less polarized.

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

sample	Molecular weight(gm/mol)	theoretical density(g/cm^3)	Experimental density(g/cm^3)	Molar volume(V_m) (cm^3/mol)
$20BaO80TeO_2$	158.346	5.680	5.61	27.878
$5Nb_2O_515BaO80TeO_2$	163.97	5.618	5.45	29.187
$10Nb_2O_510BaO80TeO_2$	169.594	5.555	5.29	30.530
$15Nb_2O_55BaO80TeO_2$	175.218	5.493	5.25	31.898

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

Sample	Theoretical optical energy gap (eV)	Experimental optical energy gap (eV)
$20BaO80TeO_2$	3.992	2.93
$5Nb_2O_515BaO80TeO_2$	3.922	2.75
$10Nb_2O_510BaO80TeO_2$	3.852	2.67
$15Nb_2O_55BaO80TeO_2$	3.785	2.58

TABLE 3. Composition , optical basicity, oxide ion polarizabilityfor all the Studied samples.

Sample	Optical basicity(A_{th})	Oxide ion polarizability (α^{02-}) $(A^0)^3$
$20BaO80TeO_2$	1.014	2.546
$5Nb_2O_5 15BaO80TeO_2$	1.005	2.511
$10Nb_2O_5 10BaO80TeO_2$	0.996	2.478
$15Nb_2O_5 5BaO80TeO_2$	0.987	2.445

The molar refraction (Rm)

The values of molar refraction for all the studied samples are listed in Table 4. It is clear, that the values of the molar refraction increase by increasing Nb_2O_5content.

The refractive index

The values of refractive index for all the studied samples are listed in Table 4. It is clear, that the values of the refractive index increaseby increasing Nb_2O_5 content as a result of increasing the values of molar volume and the values of molar refraction for all the studied samples.

The metallization criterion

From Table 5, it was found that the metallization parameter values of the present glasses decreased by increasing Nb_2O_5content and also are found to be less than one and thus all the studied samples exhibit insulating behavior [16].

The third order nonlinearsusceptibility $\chi^{(3)}$

Kim et al. [12] found that the value of third order nonlinear susceptibility for pure TeO_2(1.4x 10^{-12}esu.) . From Table 5, it is clear that the high values of third order nonlinear optical susceptibility for all the studied samples , were found to be in the range (0.7604-0.9271) x 10^{-12}esu, this means that all the studied samples are probably good candidates for nonlinear optical applications [18,19].

We have plotted the data of the 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 third order nonlinear susceptibility increases with decreasing the optical energy gap andincreasing the refractive index for all the studied samples**.**

TABLE 4.Composition , molar refraction, optical dielectric constant refactive index for all the studied samples.

Sample	Molar refraction(cm^3/mol)	Refractive index
$20BaO80TeO_2$	15.423	2.170
$5Nb_2O_5 15BaO80TeO_2$	16.262	2.185
$10Nb_2O_5 10BaO80TeO_2$	17.132	2.199
$15Nb_2O_5 5BaO80TeO_2$	18.021	2.213

TABLE 5. Composition , metallization criterion, third order nonlinear susceptibility for all the Studied samples.

Sample	The metallization criterion	(Third order nonlinear suceptibility) $\chi^3 x10^{-12}$esu.
$20BaO80TeO_2$	0.447	0.7604
$5Nb_2O_5 15BaO80TeO_2$	0.443	0.8154
$10Nb_2O_5 10BaO80TeO_2$	0.439	0.8697
$15Nb_2O_5 5BaO80TeO_2$	0.435	0.9271

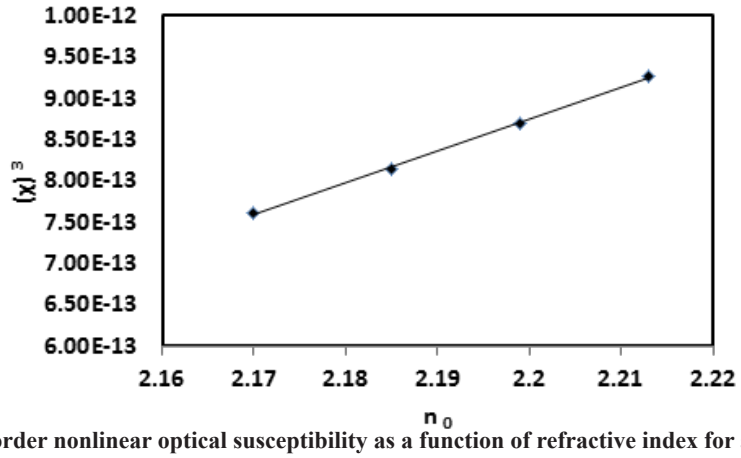

Fig. 1. The third order nonlinear optical susceptibility as a function of refractive index for all the studied samples

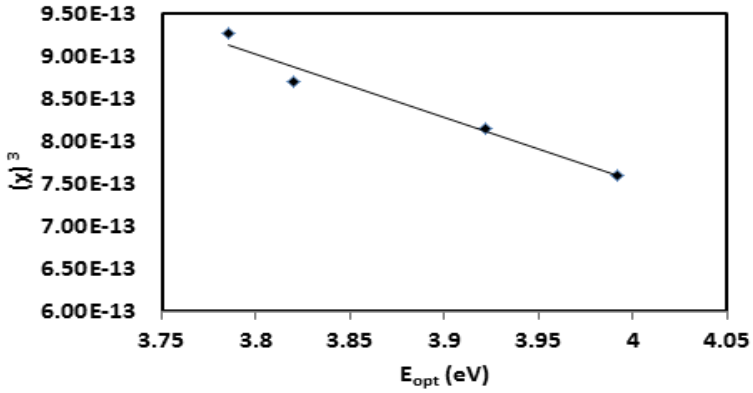

Fig. 2. Third order nonlinear susceptibility as a function of optical energy gap for all the studied samples

Conclusion

From all the above discussion, it was found that the values of density, optical energy gap, optical basicity and oxide ion polarizability, metallizationdecreaseby increasing Nb_2O_5 content. On the other hand,the values of refractive index, optical dielectric constant,molar refraction increase by increasing Nb_2O_5 content. Also, it was found thatthe values of third order nonlinear susceptibilityincrease by decreasing the optical energy gap and increasingthe refractive index. Finally,all the above values are a good basis for predicting new non linear optical materials.

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(*Received:25*/4/2018;

accepted: 10/6/2018)

الخصائص الفيزيائية Nb_2O_5 BaO TeO_2 مع تغير نسب المركب

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تأثير التباينات التركيبية على الخواص الفيزيائية مثل ، الكثافة ، الحجم المولي ، الانكسار المولي ، فجوة الطاقة البصرية ، معامل الانكسار ، الأساس البصري ، الاستقطاب الأيوني للأكسدة ، المعدنة ، والقابلية غير الخطية من الدرجة الثالثة ، معامل الانكسار اللاخطي ، مع الاختلاف في محتوى Nb_2O_5 تمت دراستها نظريا للزجاج من التركيبات xNb2O5 (٠٢-س) BaO80TeO2 (س = ٠ ، ٥ ، ٥١،٠١) وتحليل العوامل المادية المتعلقة بهذه التركيبات مع التوقعات النظرية.
تقل الكثافة المحسوبة مع زيادة محتوى Nb_2O_5 من Y 5.680 g cm^{-3}إلى5.493 g cm^{-3} ، وهذا يعني أن المصفوفة الزجاجية تصبح أقل كثافة
وجد أن فجوة الطاقة الضوئية تنخفض ، لكن مؤشر الانكسار يزداد بزيادة محتوى Nb_2O_5.
تتناقص الاستقطاب الإلكتروني لأيون أكسيد مع تناقص الأساس البصري.
توضح قيمة الأساس البصري أن المواد الزجاجية أقل أساسية.
من المقترح أنه بزيادة Nb_2O_5 ، يصبح الزجاج أقل استقطابا.
أيضا ، تم اكتشاف أن قيم القابلية غير الخطية من الدرجة الثالثة تزيد بزيادة محتوى Nb_2O_5 ووجد أنها أكبر من تلك الموجودة في زجاج السيليكا.
تم اكتشاف أن هذا الزجاج يمتلك مؤشر انكسار عالي (٣١٢,٢-٠٧١,٢) ، فجوة نطاق ضيقة نسبياً (3.992eV – 3.785eV) ، عالية الاستقطاب الإلكتروني الأيوني (-2.445 Å3 2.546 Å3) وأساسيات بصرية عالية (٤١٠,١-٧٨٩,٠).
تم العثور على أن قيم الحساسية البصرية غير الخطية من الرتبة الثالثة في النطاق (0.7604-0.9271) x10-12esu.
أخيراً ، جميع القيم المذكورة أعلاه هي أساس جيد للتنبؤ بالمواد البصرية غير الخطية الجديدة.