Journal of Fluorine Chemistry 212 (2018) 5–12

Contents lists available at ScienceDirect

Journal of Fluorine Chemistry

journal homepage: www.elsevier.com/locate/fluor

BaF_2–contained tellurite glasses: Quantitative analysis and prediction of elastic properties and ultrasonic attenuation – Part II

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ARTICLE INFO

Keywords:
BaF_2-doped tellurite glasses
Elastic properties
Ultrasonic attenuation
Rocherulle et al. model
Abd El-Moneim and Alfifi's approaches

ABSTRACT

The goal of the present paper is to complete our very recent work [J. Fluor. Chem. 210 (2018) 156–165] on the quantitative analysis and prediction of elastic properties, ultrasonic attenuation coefficient and glass transition temperature in binary BaF_2-TeO_2 glass system over the composition range 7 mol % $\leq BaF_2 \geq$ 19 mol %. All the above mentioned parameters were correlated with the ratio between packing density and mean atomic volume of the glass on the basis of Abd El-Moneim and Alfifi's approaches [2018]. In addition to this, the theoretical elastic moduli and Poisson's ratio were evaluated on the basis of the Rocherulle et al. model [1989] and compared with the corresponding experimental ones. The results show that, the ratio between packing density and mean atomic volume can be considered as a new powerful tool capable of predicting changes in ultrasonic attenuation coefficient, elastic properties and glass transition temperature. Although both the theoretical and experimental elastic moduli display the same compositional trend; a slight discrepancy between the theoretical and experimental values of shear, longitudinal and Young's moduli is observed. This discrepancy has been attributed to the anomalous behavior between various elastic properties and calculated dissociation energy per unit volume. Finally, not only Rocherulle et al. model [1989] is valid for majority of the investigated glasses, but also the correlation ratios between theoretical and experimental elastic moduli are better than those reported previously when compared the same experimental elastic moduli with the theoretically calculated ones on the basis of Makishima-Mackenzie's theory [1973, 1975].

1. Introduction

In recent years, tellurite-based glasses are studied intensively because of their various applications in electronics, nuclear and solar energy technologies, acousto-optic devices and optical fiber technology [1–6]. These glasses have several unique properties, such as good infrared transmittance, high refractive index and electrical semi-conductivity [7–11].

Fluoride-based heavy metal glasses gained much interest in the fields of fiber optics, quantum electronics and laser devices [12]. This type of glasses are known to have a wide variety of physical and optical properties such as high transparency from IR to UV region, low glass transition temperature, low linear and nonlinear refractive index, low phonon energies and their potential as host for active rare earth ions [13,14].

The choice of appropriate a glass for a particular purpose requires information about its mechanical / elastic properties. Mechanical properties, such as elastic moduli, Poisson's ratio and ultrasonic attenuation coefficient, are very informative about the structure of glasses, as they are affected by structural softening / compactness, changes in geometrical configuration, dimensionality and cross-link density due to modifier doping. The ultrasonic methods have been already proved as an effective tool to study the fundamental mechanical / elastic properties of glasses. Wei [15] studied the elastic properties of silica glass doped with different concentration of fluorine. He observed a remarkable linear decrease in the measured density, ultrasonic velocities and elastic moduli with increasing fluorine concentration. More recently, Begum and Rajendran [16,17] have studied the effect of composition from the substitution of TeO_2 by the alkaline earth fluoride BaF_2 in BaF_2-TeO_2 glasses or by the alkaline earth oxide BaO in BaO-TeO_2 glasses on the structure and properties of the tellurite network by means of XRD, SEM and DTA spectroscopes as well as the ultrasonic pulse-echo technique. The composition dependence of ultrasonic velocities and ultrasonic attenuation coefficient suggested that, both BaF_2 and BaO are incorporated the tellurite network as a glass modifier. This results in the conversion of TeO_4 trigonal bipyramids into TeO_{3+1} polyhedral and then to TeO_3 trigonal pyramids through breaking of $Te–_{eq}O_{ax}–Te$ linkages and creation of non-bridging oxygen atoms (NBOs) [2,16,17]. In the first part of this work [18], we have reported a comprehensive study on the quantitative analysis and prediction of

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https://doi.org/10.1016/j.jfluchem.2018.05.007
Received 19 March 2018; Received in revised form 17 May 2018; Accepted 17 May 2018
Available online 18 May 2018

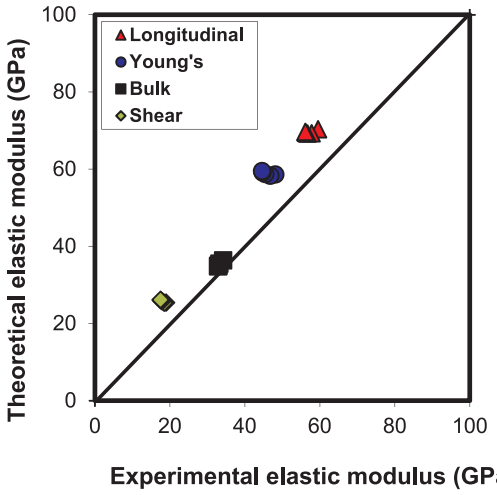

Fig. 1. Agreement between theoretical and experimental elastic moduli of binary BaF_2-TeO_2 glasses [18] on the basis of Makishima-Mackenzie's theory [20,21]. The solid line is the line of 1:1 correlation.

elastic properties and ultrasonic attenuation coefficient in binary BaF_2-TeO_2 glass system on the basis of the bond compression model [19], ring deformation model [19], Makishima-Mackenzie's theory [20,21] and Abd El-Moneim's model [22–24]. However, the following negative results were reported [18]:

i The agreement between theoretical and experimental Young's, longitudinal and shears moduli is unsatisfactory for majority of the investigated glass samples as shown in Fig.1;
ii The divergence between theoretical and experimental values increased with increasing BaF_2 content in the glass; and
iii The behavior of all elastic properties with the calculated dissociation energy per unit volume of the glass is against Makishima-Mackenzie's theory [20,21].

However, Rocherulle et al. [25] have made an attempt to improve the agreement between the theoretical and experimental elastic moduli of multi-component oxide glasses; especially those have values of elastic moduli greater than 100 GPa. They made some modifications in the expression of the packing density and reported very good agreement between the theoretical and experimental elastic moduli. Very recently, Abd El-Moneim and Alfifi [26] have also been reported two new semi-empirical formulas, which correlate both the ultrasonic attenuation coefficient and bulk modulus with the ratio between packing density and mean atomic volume of the glass. The same authors [26] have verified the applicability of their semi-empirical formulas for PbO-P_2O_5, V_2O_5-P_2O_5, CuO-P_2O_5, Cr_2O_3-doped Na_2O-ZnO-P_2O_5 and Ag_2O-V_2O_5-TeO_2 glass systems.

As far the author knows, the applicability of Abd El-Moneim and Alfifi's semi-empirical formulas [26] and Rocherulle et al. model [25] has not been demonstrated for the BaF_2-doped tellurite glasses. Therefore, the present study had the following objectives:

i To analyze and predict the composition dependence of ultrasonic attenuation coefficient, elastic properties and glass transition temperature in BaF_2-TeO_2 glasses on the basis of Abd El-Moneim and Alfifi's approaches [26]. The correlations between all these parameters and the ratio between packing density and mean atomic volume were studied;
ii To testify the applicability of Rocherulle et al. model [25] for the investigated BaF_2-TeO_2 glass samples. The theoretical values of elastic moduli and Poisson's ratio were calculated from the dissociation energy per unit volume and packing density and compared with the corresponding experimental values.

2. Theory

The elastic properties and ultrasonic attenuation coefficient of a glass are affected by several different structural aspects. At the atomic scale, these parameters are closely related to the mean atomic volume and packing density. Nonetheless, in the past years, various simplest theoretical models were developed to predict the ultrasonic attenuation coefficient and to estimate various elastic properties of glasses based only on their chemical compositions. Among of these approaches, the presumably most frequently applied models were those proposed by Makishima and Mackenzie [20,21], Rocherulle et al. [25] and Abd El-Moneim and Alfifi [26].

2.1. Abd El-Moneim and Alfifi's approach [26] to ultrasonic attenuation coefficient and bulk modulus

In the first part of the present study [18], we expressed the ultrasonic attenuation coefficient of glassy materials on the basis of Rajendran et al. [27] suggestions as:

$$\alpha = a_1\alpha_a + \alpha_c \tag{1}$$

where a_1 is a constant, whereas α_a and α_c are the true absorption and coupling loss between the sample and ultrasonic transducer, respectively.

Very recently, Abd El-Moneim and Alfifi [26] reported the semi-empirical formula (2), which correlates the experimentally measured ultrasonic attenuation coefficient at room temperature with the ratio between mean atomic volume and packing density of the glass;

$$\text{Ultrasonic attenuation coefficient } \alpha = \chi / (V_t/\overline{V})^{\beta} \tag{2}$$

$$\text{Packing density } V_t = \frac{1}{V_M}\sum_i x_i V_i \tag{3}$$

$$\text{Mean atomic volume } \overline{V} = V_M/\psi \tag{4}$$

$$\text{Molar volume } V_M = \sum_i x_i M_i/\rho \tag{5}$$

Packing factor for a glass component i in the form A_aB_b

$$V_i = 4\pi N_a (a R_A^3 + b R_B^3)/3 \tag{6}$$

where χ and β are two constants, their values depend upon the glass composition and applied ultrasonic frequency, whereas N_a, ρ and ψ are Avogadro's number, glass density and total number of atoms in the glass formula, respectively. On the other hand, x_i and M_i are the respective molar fraction and molecular weight of a glass component i, which have cation A and anion B with respective Pauling's ionic radii R_A and R_B. The advantage of Eq. (2) is that the ultrasonic attenuation coefficient is now expressed in terms of two compositional parameters, which are relatively easy to estimate from chemical composition of the glass compared with the calculation of the dissociation energy per unit volume (G_t) and average first-order stretching force constant (F) of the glass, which were appeared a semi-empirical relationship reported previously by Abd El-Moneim [23] in the form;

$$\alpha = \frac{\chi'}{F}(F/10G_tV_t^2)^{m/n} \tag{7}$$

where χ' is another constant, its values also depends upon the applied frequency and composition of the glass, whereas m and n are two positive powers, their values depends upon the glass-forming systems and their compositions.

Bulk modulus is defined as the ratio between isotropic pressure and relative volume change. On the basis of Abd El-Moneim and Alfifi's approaches [26], the bulk modulus of the glass can be expressed in terms of the ratio between mean atomic volume and packing density according to the following semi-empirical formula;

$$K = Q\ (V_t/\overline{V})^{\gamma} \quad (8)$$

where Q and γ are two new constants their values depend upon the type of the glass and its composition.

2.2. Rocherulle et al. model [25] for elastic moduli and Poisson's ratio

Rocherulle et al. [25] tried to improve the agreement between theoretical and experimental elastic moduli of glasses; especially those have values of elastic moduli greater than 100 GPa. They made a modification in the expression of Makishima-Mackenzie's packing density [20,21] and reported the following semi-empirical equations, which relate the theoretical elastic moduli and Poisson's ratio of multi-component oxide glasses with the packing density and dissociation energy per unit volume;

$$\text{Young's modulus } E^*_{th} = 8.36\ C_t G_t \quad (9)$$

$$\text{Bulk modulus } K^*_{th} = 10.0\ C_t^2\ G_t \quad (10)$$

$$\text{Shear modulus } S^*_{th} = 3\ K^*_{th}/(10.2\,C_t - 1) \quad (11)$$

$$\text{Longitudinal modulus } L^*_{th} = K^*_{th} + 4S^*_{th}/3 \quad (12)$$

$$\text{Poisson's ratio } \mu^*_{th} = 0.5 - (1/7.2\ C_t) \quad (13)$$

$$\text{Packing density} C_t = \sum_i x_i\ V_i\ \rho_i/M_i \quad (14)$$

Dissociation energy per unit volume

$$G_t = \sum_i x_i\ G_i \quad (15)$$

Dissociation energy per unit volume for a glass component i

$$G_i = \rho_i U_i/M_i \quad (16)$$

where ρ_i and U_i are the respective density and molar dissociation energy of a glass component i. The semi-empirical Eqs. from (9) to (12) give the values of theoretical elastic moduli in GPa if the unit of G_t is kcal/cm^3.

3. Experimental

The various techniques for preparation of the investigated BaF_2-TeO_2 and BaO-TeO_2 glass samples, measurement of density, ultrasonic velocities and attenuation coefficient and determination of the glass transition temperature were described in the earlier studies of Begum and Rajendran [16,17]. Al the ultrasonic measurements were carried out at room temperature and at 5 MHz frequency. The overall accuracy in density, ultrasonic velocity and ultrasonic attenuation coefficient measurements is ± 0.5 Kgm^{-3}, ± 5% and ± 2%, respectively [16,17].

4. Results and discussion

It is a well-known fact that, the network of pure tellurite glass is basically composed of TeO_4 trigonal bipyramids, which are connected to each other through the covalent Te–$_{eq}O_{ax}$–Te linkages, where $_{eq}O$ refers to oxygen in an equatorial plane and O_{ax} refers to oxygen in axial position with respect to the Te atom [10]. In addition to this, each TeO_4 trigonal bipyramid has a lone pair of electrons in one of its equatorial sites [10]. The addition of a modifier to vitreous TeO_2 is expected to modify the network structure and changes all the physical and elastic properties of the glass. The type of modification depends upon the nature and concentration of the added modifier. The binary BaF_2-TeO_2 glasses studied in the present work are listed in Table 1 together with their compositions, ultrasonic properties and ultrasonic attenuation coefficient [16]. The literature available [16,18] on these glasses indicates that all the added molar fractions of the alkaline earth fluoride BaF_2 are consumed in the transformation of TeO_4 trigonal bipyramids into TeO_3 trigonal pyramids through breaking of Te–$_{eq}O_{ax}$–Te linkages and creation of non-bridging oxygen atoms (NBOs) (two NBOs for each Ba^{2+} ion). Thus, the progressive increase in BaF_2 and expense of TeO_2 is expected to increase the number of NBOs, which consequently reduces the rigidity and compactness of BaF_2-TeO_2 glasses in comparison with the parent pure TeO_2 glass. However, in Ref. [18], we have calculated the number of network bonds per unit volume, average cross-link density and bond compression bulk modulus for the same present BaF_2-TeO_2 glasses from the bond compression model [19]. The results reveal that all these parameters show a gradual decrease with increasing BaF_2 concentration.

The calculated values of packing density on the basis of Makishima-Mackenzie's theory [20,21], beside those of the mean atomic volume are given in Table 2 for BaF_2-TeO_2 glass system under investigation. The necessary factors for calculating these parameters are given in Table 3. As clearly seen from this Table 2, the addition of the alkaline earth fluoride BaF_2 alters both the packing density and mean atomic volume. Increasing of BaF_2 from 7 to 19 mol% decreases the packing density from 0.5189 to 0.4896 and increases the mean atomic volume from 9.33 to 9.68 cm^3/mol. The gradual decrease in the packing density with the substitution of TeO_2 by BaF_2 is related to the reduction in the rigidity and elastic stiffness of the glass due to the modifier role of BaF_2 as suggested by Makishima and Mackenzie [20,21].

The modifier role of the alkaline earth fluoride BaF_2 in the present BaF_2-TeO_2 glasses can also be understood from the variation of the mean atomic volume as follows. The increase in the mean atomic volume with the concurrent addition of BaF_2 and reduction of TeO_2 is expected to decrease the total number of atoms per unit volume of the glass ($\psi\ N_a/V_M$), which consequently weakness and loose packing the structure in its resistance to compression as evidenced by the decrease of elastic moduli (Fig. 2) and glass transition temperature (Fig. 3) and increase of Poisson's ratio (Fig. 4). The increase in the ultrasonic attenuation coefficient supports the so-called open (loose packing and weak) structure of BaF_2-TeO_2 glasses with the substitution of TeO_2 by BaF_2. This discussion is in accordance with that reported in Ref. [18] when interpreting the compositional dependence of molar volume, packing density, fractal bond connectivity, average cross-link density, number of network bonds per unit volume, bond compression bulk modulus and mean atomic ring in the same glasses [18].

According to Abd El-Moneim and Alfifi's approaches [26], the ultrasonic attenuation coefficient and elastic moduli of glasses depend strongly upon the ratio between packing density and mean atomic volume. Thus, it is very important to testify these approaches [26] for the present BaF_2-TeO_2 glasses as follows.

4.1. Correlation between ultrasonic attenuation coefficient and the ratio between packing density and mean atomic volume

Ultrasonic attenuation coefficient describes the total reduction in sound intensity due to absorption of energy by the medium and the deflection of energy from the path of the beam by reflection, refraction and scattering [22]. The semi-empirical formula (2) suggested that, at a fixed frequency, a plot of ultrasonic attenuation coefficient versus the ratio between packing density and mean atomic volume ($V_t/\overline{V}$) would yield an inverse proportionality. It is quite clear from Fig. 5 that, this is true for the present BaF_2-TeO_2 glasses at 5 MHz frequency. The least-square linear regressions performed on $\log(\alpha)$ and $\log(V_t/\overline{V})$ yield the following semi-empirical relationship for ultrasonic attenuation coefficient

$$\alpha = 6.516 \times 10^{-6}/(V_t/\overline{V})^{3.933} \quad (17)$$

with correlation ratio of 98.4%, $\chi = 6.516 \times 10^{-6}$ and $\beta = 3.933$. These results reveal that, the ratio between packing density and mean atomic volume play a dominate role in understanding and predicting changes in the ultrasonic attenuation coefficient of BaF_2-TeO_2 glasses.

Previous studies [2,16–18] showed that, both BaF_2 and barium oxide BaO are incorporated the tellurite network as a glass modifier.

Table 1
Compositions, density, elastic properties, ultrasonic attenuation coefficient and glass transition temperature of binary BaF_2-TeO_2 glass system [16].

T_g (K)	μ	E (GPa)	K (GPa)	L (GPa)	S (GPa)	α_{5MHz} (dB/cm)	ρ (g/cm^3)	BaF_2 (mol %)	BaF_2 (wt %)
593	0.2654	48.09	34.20	59.5	19.0	0.57	5.7437	07	08
591	0.2646	46.79	33.20	57.8	18.5	0.62	5.6698	09	10
587	0.2693	45.44	32.90	56.7	17.9	0.75	5.6198	14	15
583	0.2700	44.70	32.89	56.3	17.6	0.79	5.6028	17	18
580	0.2733	44.57	32.83	56.1	17.5	0.81	5.6008	19	20

Table 2
Compositional and theoretical elastic properties of binary BaF_2-TeO_2 glass system.

K_{bc}[18] (GPa)	μ^*_{th}	E^*_{th} (GPa)	K^*_{th} (GPa)	L^*_{th} (GPa)	S^*_{th} (GPa)	G_t[18] (kcal/cm^3)	C_t	$\overline{V}$ (cm^3/mol)	V_t[18]	BaF_2 (mol %)
73.25	0.2273	57.56	35.07	68.43	25.08	13.52	0.5093	9.33	0.5189	07
69.73	0.2254	57.88	35.01	68.61	25.26	13.69	0.5057	9.47	0.5095	09
59.19	0.2202	58.56	34.77	68.91	25.67	14.11	0.4964	9.60	0.4981	14
58.90	0.2171	58.99	34.64	69.13	25.93	14.37	0.4910	9.65	0.4925	17
56.34	0.2150	59.23	34.53	69.23	26.09	14.54	0.4873	9.68	0.4896	19

Table 3
Different parameters for glass components TeO_2, BaO and BaF_2 [18,28].

G_i (kcal/cm^3)	C_i	V_i (cm^3/mole)	ρ_i (g/cm^3)	M_i (g/mol)	Glass component
12.92	0.5222	14.70	5.670	159.6	TeO_2
9.70	0.4887	13.10	5.720	153.33	BaO
12.92	0.3385	12.13	4.893	175.34	BaF_2

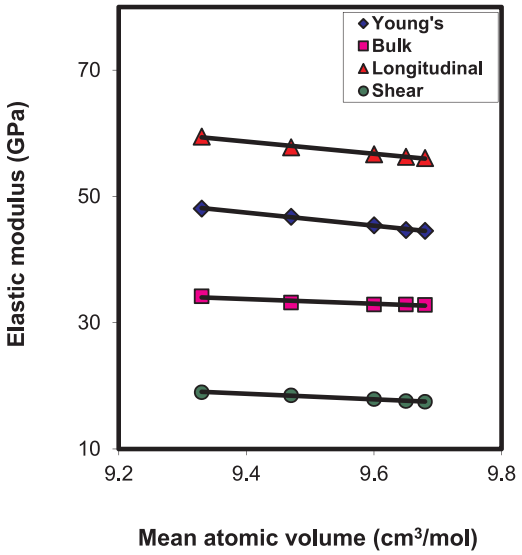

Fig. 2. Dependence of elastic moduli on mean atomic volume in binary BaF_2-TeO_2 glass system. The solid lines represent the least-square fitting of the data.

Thus, it is worth examining the validity of the same semi-empirical formula (2) for the binary BaO-TeO_2 glass system. The applied experimentally measured data of ultrasonic attenuation coefficient at room temperature and at 5 MHz frequency are listed in Table 4 for the investigated BaO-TeO_2 glass samples. The calculated values of packing density and mean atomic volume are listed in the same table. The applied values of V_i and M_i for BaO oxide are given in Table 3. Fig. 6 illustrates how the ultrasonic attenuation coefficient varies with the ratio $(V_t/\overline{V})$ in BaO-TeO_2 glasses at 5 MHz frequency. For comparison, the data of the present BaF_2-TeO_2 glasses are included in the same figure. It

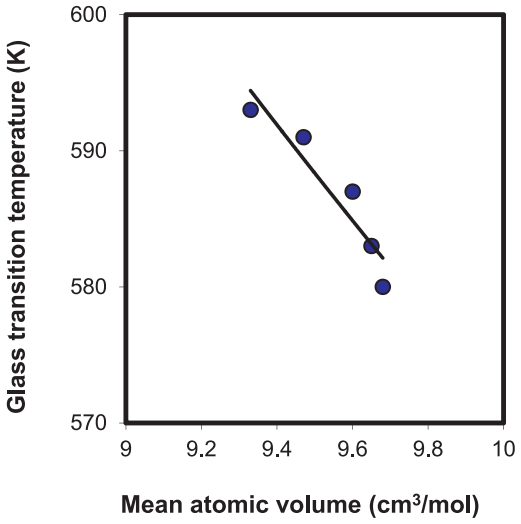

Fig. 3. Dependence of glass transition temperature on mean atomic volume in binary BaF_2-TeO_2 glass system. The solid line represents the least-square fitting of the data.

is clear from this figure that, for both BaO-TeO_2 and BaF_2-TeO_2 glasses, the ultrasonic attenuation coefficient shows a systematic decrease as the $(V_t/\overline{V})$ ratio is increased. In addition to this, the fitted curve to the data of BaO-TeO_2 glasses is shifted towards lower values of ultrasonic attenuation coefficients. In case of BaO-TeO_2 glasses, the least-square linear regressions performed on $\log(\alpha)$ and $\log(V_t/\overline{V})$ yield the following semi-empirical relationship for the ultrasonic attenuation coefficient at 5 MHz frequency;

$$\alpha = 19.186 \times 10^{-6} / (V_t/\overline{V})^{3.42} \quad (18)$$

with correlation ratio of 75%, $\chi = 19.186 \times 10^{-6}$ and $\beta = 3.42$. These results proved that the semi-empirical formula (2) also satisfies the data of BaO-TeO_2 glasses very well. It noticeable that, although both BaF_2-TeO_2 and BaO-TeO_2 glasses have a very close values of β, they have two different values of χ. BaO-TeO_2 glasses have value of χ greater than three times that of BaF_2-TeO_2 glasses. These results are reasonable and agree with Abd El-Moneim and Alfifi's approaches [26]. However, the applicability of the semi-empirical formula (2) was verified very recently for PbO-P_2O_5 and CuO-P_2O_5 glasses at 10 MHz frequency, for V_2O_5-P_2O_5 glasses at 8 MHz frequency, for Cr_2O_3-doped Na_2O-ZnO-

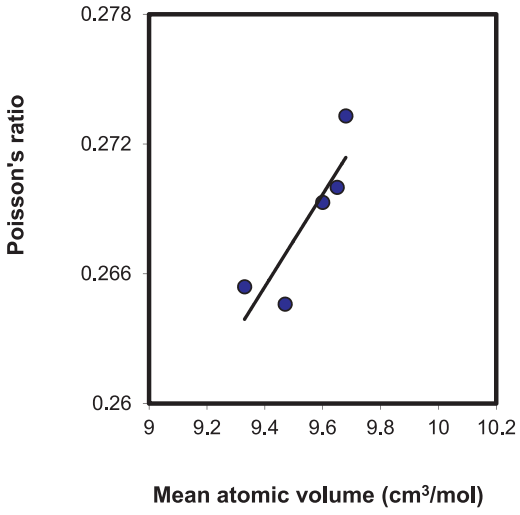

Fig. 4. Dependence of Poisson's ratio on mean atomic volume in binary BaF_2-TeO_2 glass system. The solid line represents the least-square fitting of the data.

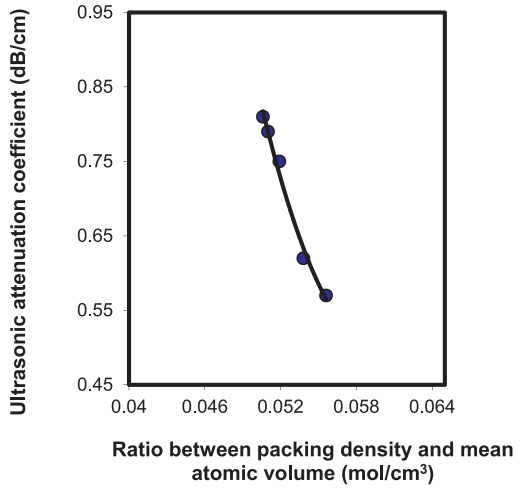

Fig. 5. Relation between ultrasonic attenuation coefficient and the ratio between packing density and mean atomic volume glasses at 5 MHz in binary BaF_2-TeO_2 glass system. The solid line represents the least-square fitting of the data.

P_2O_5 glasses at 5 MHz frequency and for Ag_2O-V_2O_5-TeO_2 glasses at 4 MHz frequency [26]. The reported values of χ and β for these glasses, along with those obtained in the present study for BaF_2-TeO_2 and BaO-TeO_2 glasses are summarized in Table 5. From this table, we concluded that, for a given frequency, the values of χ and β depend strongly upon the type of the glass and its composition. This supports Abd El-Moneim and Alfifi's approaches [26] and confirms the validity of the semi-empirical formula (2) for the phosphate- and tellurite-based glasses.

4.2. Correlating the elastic properties and glass transition temperature with the ratio between packing density and mean atomic volume

Fig. 7 shows how the experimental bulk modulus varies with the ratio $(V_t/\overline{V})$ in the same binary BaF_2-TeO_2 glass system under investigation. The forward proportionality between bulk modulus and the ratio $(V_t/\overline{V})$ clarifies that the semi-empirical Eq. (8) satisfies the data of these glasses very well. The equation of the fitted curve can be represented by the semi-empirical formula;

$$K = 108.1\ (V_t/\overline{V})^{0.4} \quad (19)$$

with correlation ratio of 85%, $Q = 108.1$ and $\gamma = 0.4$. These results suggest that the compositional dependence of bulk modulus in BaF_2-TeO_2 glasses is predictable from Abd El-Moneim and Alfifi's approaches [26]. As expected, the obtained values of values of Q and γ for BaF_2-TeO_2 glasses are different from those reported very recently for PbO-P_2O_5, V_2O_5-P_2O_5 or the Cr_2O_3-doped Na_2O-ZnO-P_2O_5 glass systems as shown in Table 5. Fig. 8 illustrates how the bond compression bulk modulus (K_{bc}) varies with the ratio between packing density and mean atomic volume in the same present BaF_2-TeO_2 glasses. The data of K_{bc} were taken from our previous study on the same glasses [18]. The dependence of the bond compression bulk modulus on the ratio between packing density and mean atomic volume was fitted into a power semi-empirical relation $K_{bc} = 30.599 \times 10^3 (V_t/\overline{V})^{2.88}$ with correlation ration of 95.6%.

It is a well-known fact that, the glass transition temperature and Poisson's ratio reflect changes in the coordination number of the network forming atoms and destruction of the network structure brought about by the formation of NBOs in glasses. Thus, the composition dependence of these two parameters helps to reveal the loosely packed structure of the glass. Loosely packed glasses are expected to have lower glass transition temperature and higher Poisson's ratio compared with closely packed ones. In the light of this, the modifier role of BaF_2 in the present BaF_2-TeO_2 glasses and that of BaO in BaO-TeO_2 glasses can be further support by correlating - the glass transition temperature and Poisson's ratio of these glasses with the ratio between packing density and mean atomic volume as follows:

i Fig. 9 shows the dependence of glass transition temperature (T_g) on the ratio $(V_t/\overline{V})$ in BaF_2-TeO_2 and BaO-TeO_2 glasses. The applied data of T_g were taken from Refs. [16,17]. The figure reveals clearly that, for both BaF_2-TeO_2 and BaO-TeO_2 glass systems; there is a rapid increase in the glass transition temperature with increasing the ratio $(V_t/\overline{V})$. The relationship between glass transition temperature and $(V_t/\overline{V})$ can be represented by the following semi-empirical equation;

$$T_g = P\ (V_t/\overline{V})^{\delta} \quad (20)$$

where P and δ are two constants, their values depend upon the type of the glass and its composition. The equations of the fitted curves to the data of BaF_2-TeO_2 and BaO-TeO_2 glasses can be represented by the respective semi-empirical formulas (21) and (22),

Table 4
Compositions, density, ultrasonic attenuation coefficient, packing density, mean atomic volume and glass transition temperature of binary BaO-TeO_2 glass system.

μ[17]	T_g[17] (K)	$\overline{V}$ (cm^3/mol)	V_t	α_{5MHz}[17] (dB/cm)	ρ[17] (g/cm^3)	BaO	
						(mol %)	(wt %)
0.2630	599	9.69	0.51673	0.45	5.646	9.3	9
0.2653	591	9.78	0.51552	0.46	5.645	12.4	12
0.2694	585	9.93	0.51139	0.46	5.613	15.5	15
0.2740	580	10.07	0.50790	0.49	5.587	18.5	18
0.2764	576	10.15	0.50690	0.54	5.584	20.6	20
0.2779	579	10.22	0.50606	0.61	5.583	22.7	22

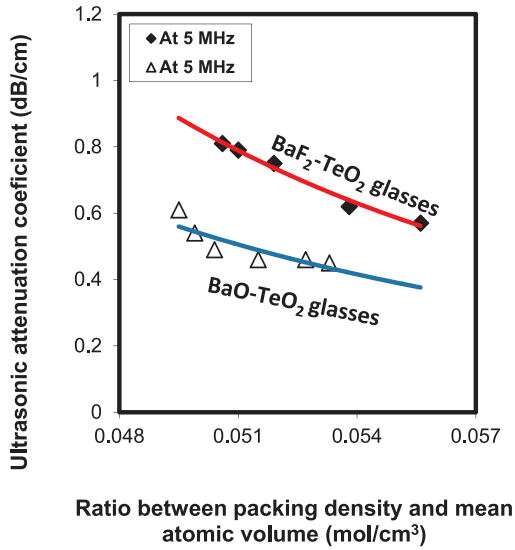

Fig. 6. Relation between ultrasonic attenuation coefficient and the ratio between packing density and mean atomic volume glasses at 5 MHz in (◆) BaF_2-TeO_2 glasses and (Δ) BaO-TeO_2. The solid lines represent the least-square fitting of the data.

Table 5
Values of the constants χ, Q, β and γ for different glass systems.

Glass system	Frequency (MHz)	Using Eq. (2)		Using Eq. (8)		Ref.
		χ	β	Q	γ	
BaF_2-TeO_2	5	6.516×10^{-6}	3.933	108.1	0.40	Present study
BaO-TeO_2	5	19.186×10^{-6}	3.420	–	–	Present study
CuO-P_2O_5	10	80.00×10^{-3}	1.510	–	–	[26]
PbO-P_2O_5	10	1.11×10^{-5}	4.843	1272	1.44	[26]
V_2O_5-P_2O_5	8	3.98×10^{-12}	9.763	884	1.25	[26]
Ag_2O-V_2O_5-TeO_2	4	4.40×10^{-9}	7.229	–	–	[26]
Cr_2O_3-doped Na_2O-ZnO-P_2O_5	5	5.20×10^{-3}	2.619	4752	4.77	[26]

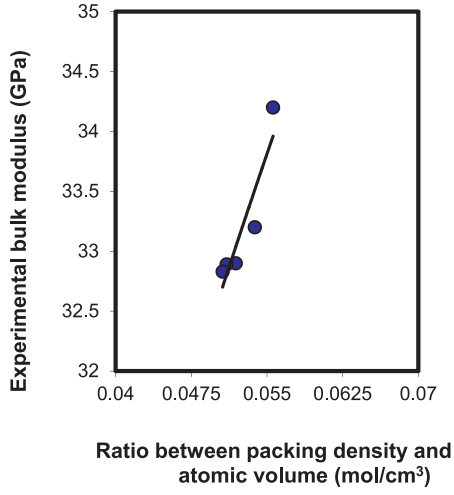

Fig. 7. Relation between experimental bulk modulus and the ratio between packing density and mean atomic volume in binary BaF_2-TeO_2 glass system. The solid line represents the least-square fitting of the data.

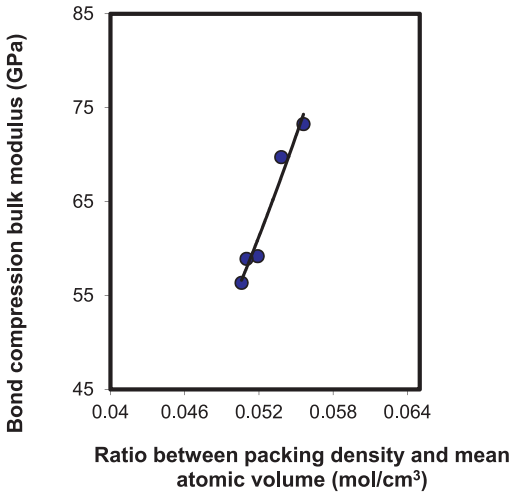

Fig. 8. Relation between bond compression bulk modulus and the ratio between packing density and mean atomic volume in binary BaF_2-TeO_2 glass system. The solid line represents the least-square fitting of the data.

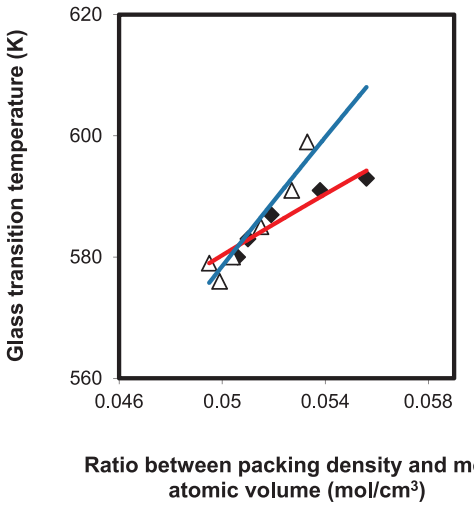

Fig. 9. Relationship between glass transition temperature and the ratio between packing density and mean atomic volume in (◆) BaF_2-TeO_2 glasses and (Δ) BaO-TeO_2 glasses. The solid lines represent the least-square fitting of the data.

$$T_g = 1134(V_t/\overline{V})^{0.223} \quad (21)$$

with correlation ratio of 91.7%, $P = 1134$ and $\delta = 0.223$;

$$T_g = 2359(V_t/\overline{V})^{0.469} \quad (22)$$

with correlation ratio of 92.1%, $P = 2359$ and $\delta = 0.469$. According to these results, BaO-TeO_2 glasses have values of P and δ greater than twice those of BaF_2-TeO_2 glasses. The dependence of P and δ the nature of the added modifier supports Abd El-Moneim and Alfifi's approaches [26].

ii Fig. 10 demonstrates the relationship between Poisson's ratio and $(V_t/\overline{V})$ ratio in the same studied BaF_2-TeO_2 and BaO-TeO_2 glass systems. The inverse proportionality between Poisson's ratio and $(V_t/\overline{V})$ agrees with Abd El-Moneim and Alfifi's approaches [26]. These results suggest that Poisson's ratios of BaF_2-TeO_2 and BaO-TeO_2 glasses are also predictable the ratio between packing density and mean atomic volume. The equations of the fitted curves can be represented by the semi-empirical formula

$$\mu = R/(V_t/\overline{V})^{\lambda} \quad (23)$$

where R and λ are two constants, their values depend upon the type

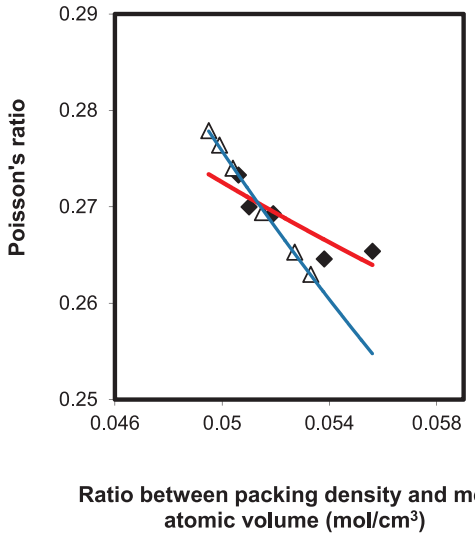

Fig. 10. Relationship between Poisson's ratio and the ratio between packing density and mean atomic volume in (♦) BaF_2-TeO_2 glasses and (Δ) BaO-TeO_2 glasses. The solid lines represent the least-square fitting of the data.

of the glass and its composition. The least-square linear regressions performed on $\log(\mu)$ and $\log(V_t/\overline{V})$ yield the respective semi-empirical relationships (24) and (25) for BaF_2-TeO_2 and BaO-TeO_2 glasses;

$$\mu = 0.11\,/(V_t/\overline{V})^{0.30} \tag{24}$$

with correlation ratio of 80.2%, $R = 0.11$ and $\lambda = 0.30$;

$$\mu = 0.029\,/(V_t/\overline{V})^{0.74} \tag{25}$$

with correlation ratio of 92.1%, $R = 0.029$ and $\lambda = 0.74$. In compared to BaF_2-TeO_2 glasses, BaO-TeO_2 glasses have higher value of λ and smaller value of R. This confirms that Poisson's ratios of these glasses are predictable from the ratio between packing density and mean atomic volume. This discussion agrees very well with prediction of the same data of Poisson's ratio from the average cross-link density [18].

4.3. Agreement between theoretical and experimental elastic moduli on the basis of Rocherulle et al. model [25]

It is important to compare between the experimentally measured elastic moduli and Poisson's ratio of BaF_2-TeO_2 glasses with those theoretically calculated on the basis of Rocherulle et al. model [25]. The calculated values of packing density on the basis of Rocherulle et al. model [25], beside those of dissociation energy per unit volume, elastic moduli and Poisson's ratio are listed in Table 2 for all BaF_2-TeO_2 glass samples under investigation. The necessary factors for calculating both the packing density and dissociation energy per unit volume of the glass are given in Table 3 [18,28]. At first glance, the values of C_t follow the same compositional dependency which was seen before in the experimental data of elastic moduli [16,18]. This is in accordance with Rocherulle et al. [25] suggestions. The relationship between the theoretical and experimental elastic moduli of BaF_2-TeO_2 glasses is illustrated in Fig. 11. From the figure, we concluded that:

i The theoretically calculated values of bulk modulus on the basis of Rocherulle et al. model [25] are in excellent agreement with the corresponding experimental values. The correlation ratio between the theoretical and experimental values ranges between 98% and 95%;
ii There is a reasonable agreement between the theoretical and experimental values of longitudinal and Young's moduli. The correlation ratio ranges between 87% and 81% for longitudinal modulus and between ranges 84% and 75.2% for Young's modulus;
iii The agreement between theoretical and experimental values of shear modulus is unsatisfactory for all samples. The correlation ratio and between 76% and 67.1%.

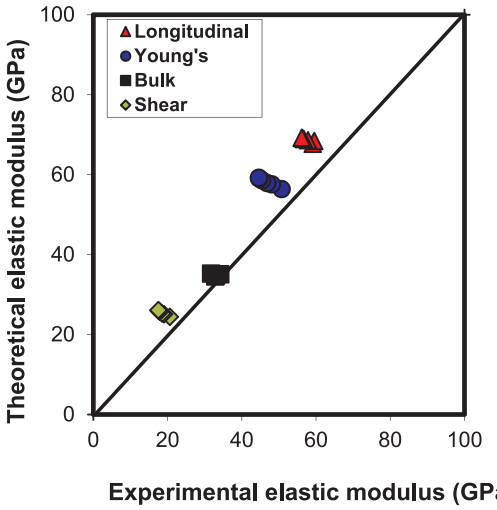

Fig. 11. Agreement between theoretical and experimental values of elastic moduli in binary BaF_2-TeO_2 glass system on the basis of Rocherulle et al. model [25]. The solid line is the line of 1:1 correlation.

However, in Ref. [18], we studied the agreement between the theoretical and experimental moduli elastic of the same studied BaF_2-TeO_2 glasses on the basis of Makishima-Mackenzie's model [20,21]. The correlation ratios between the theoretical and experimental values were found to be range between 94.2% and 93.4% for bulk modulus, between 86% and 81% for longitudinal modulus, between 82% and 75% for Young's modulus and between 75% and 67% for shears modulus. These results reveal that the model of Rocherulle et al. model [25] is more suitable than Makishima-Mackenzie's theory [20,21] for predicting the elastic moduli of the studied BaF_2-TeO_2 glasses. On the basis of Rocherulle et al. model [25], the agreement between theoretical and experimental values of Poisson's ratio was found to be ranges between 86% and 79%. These correlation ratios are very close to those reported previously for the same glasses [18] on the basis of Makishima-Mackenzie's model [20,21], which ranges between 87.6% and 79.1%.

One interesting observation in Fig. 11 is that, the theoretically calculated values of elastic moduli for all the investigated BaF_2-TeO_2 glass samples are greater than the corresponding experimental values. Moreover, the divergence between the theoretical and experimental values of elastic moduli and Poisson's ratio was found to be increases with increasing BaF_2 concentration in the glass (see Tables 1 and 2). This can be explained as follows: Based on the modifier role of the alkaline earth fluoride BaF_2 in the investigated BaF_2-TeO_2 glasses, the dissociation energy per unit volume of TeO_2 oxide was expressed as [18]

$$G_{TeO_2} = N_4\,G_4 + (1 - N_4)\,G_3 \tag{26}$$

where G_4 and G_3 are the respective dissociation energy per unit volume for TeO_4 and TeO_3 structural units, while N_4 is the fraction of TeO_4 structural units in the glass. However, in the present calculation, we have ignored the presence of TeO_3 structural units and used the dissociation energy of 54 kJ/ cm^3 [28] for TO_4 groups, which has been determined empirically from Young's modulus of pure TeO_2 glass. This is because the concentration and dissociation energy per unit volume of the TeO_3 structural units are unknown so far. In addition to this, the experimental elastic moduli show opposite behavior with the calculated dissociation energy per unit volume of the glass as shown in Table 2.

This is against Rocherulle et al. model [25] and reflects in the divergence between the theoretical and experimental values of elastic moduli and Poisson's ratio.

From the above discussion, it can be concluded that the best correlation between experimental and theoretical elastic moduli and Poisson's ratio of BaF_2-TeO_2 glasses on the basis of Rocherulle et al. model [25] or Makishima-Mackenzie's theory [20,21] requires knowing the appropriate values of G_t and V_t for each investigated glass sample. Considering the effect of all the structural units, it is first necessary to identify all the types of bonds present in the prepared glass and then to ascribe appropriate values of G_i and V_i for each type of bonds by using neutron diffraction, Raman EXAFS and FTIR data. Thus, taking into account the effect of the basic structural units that present in the glass network as well as the uncertainty inherent in experimental measurements, we believe that both Makishima-Mackenzie's [20,21] and Rocherulle et al. models [25] are valid for the all the studied BaF_2-TeO_2 glasses and give good agreement between the calculated and observed values of elastic moduli and Poisson's ratio.

5. Conclusions

A comprehensive study has been carried out on the prediction of ultrasonic attenuation coefficient, elastic properties and glass transition temperature in binary BaF_2-TeO_2 glass system. All the above mentioned parameters were correlated with the ratio between packing density and mean atomic volume of the glass on the basis of Abd El-Moneim and Alfifi's approaches [26]. The theoretical elastic moduli and Poisson's ratio have also been evaluated on the basis of Rocherulle et al. model [25] and compared with the corresponding experimental ones. The major conclusions can be summarized as follows:

i The ratio between packing density and mean atomic volume can be considered as a new powerful tool capable of predicting the compositional dependence of ultrasonic attenuation coefficient, elastic properties and glass transition temperature in BaF_2-TeO_2 glasses;
ii Although both the theoretical and experimental elastic moduli display the same compositional trend, a discrepancy between the theoretical and experimental values of shear, longitudinal and Young's moduli is observed. This discrepancy has been interpreted in terms of the anomalous behavior between elastic moduli and calculated dissociation energy per unit volume of the glass; and
iii In compared to Makishima-Mackenzie's theory [20,21], Rocherulle et al. model [25] appears to be more suitable for predicting the experimental data of elastic moduli.

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