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Theoretical analysis for ultrasonic properties of vanadate-phosphate glasses over an extended range of composition: Part I

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ABSTRACT

Effect of V_2O_5 on the physical, structural and ultrasonic properties of binary V_2O_5-P_2O_5 glasses has been comprehensively interpreted over a wide range of composition (45 mol% ≥ V_2O_5 ≤ 85 mol%). Elastic moduli and ultrasonic attenuation coefficient were correlated with the most significant compositional parameters, such as molar volume, excess molar volume, number of network bonds per unit volume, oxygen density, first-order stretching force constant, single bond strength, dissociation energy per unit volume and packing density of the glass. The correlation has been carried out on the basis of Abd El-Moneim's semi-empirical formulas, bond compression model and Makishima-Mackenzie's theory. One of Abd El-Moneim's semi-empirical formulas was modified, due to the anomalous behavior between ultrasonic properties and calculated dissociation energy per unit volume. On the basis of the modified semi-empirical formula, correlation between ultrasonic attenuation coefficient and molar volume is achieved through the average first-order stretching force constant of P-O-V linkages. The divergence between theoretical and experimental values of elastic moduli has been attributed to the anomalous behavior between ultrasonic properties and dissociation energy per unit volume of the glass.

1. Introduction

Ultrasonic properties play a significant role in understanding the structural characteristics of the glass network. A review of literature indicates that extensive studies have been made on the measurement of elastic moduli, Poisson's ratio and ultrasonic attenuation coefficient in different types of inorganic oxide glasses as a function of composition, frequency and temperature, using ultrasonic techniques [1–17]. The composition dependence of elastic moduli and Poisson's ratio has been quantitatively analyzed and predicted in a variety of inorganic oxide glasses [2,3,7–9,12,13–32], on the basis of the bond compression and ring deformation models [19] as well as Makishima and Mackenzie's theory [20,21]. Results revealed that elastic moduli and Poisson's ratio are very informative about the structure of glasses because they are directly related to microscopic properties through the behavior of the network former and modifier.

On contrast, correlation between ultrasonic attenuation coefficient and structural parameters of glasses has not been received a suitable attention until 2006. Very recently, the author reported a number of extensive studies deal with prediction of ultrasonic attenuation coefficient in inorganic oxide glasses [33–38]. A model of three semi-empirical formulas, known as Abd El-Moneim's model [33,35], was reported. On the basis of this model, the experimentally measured ultrasonic attenuation coefficient at room temperature (α) is related to oxygen density ($[O]$), average first-order stretching force constant (F), means atomic ring size (ℓ), dissociation energy per unit volume (G_t), packing density (V_t) and observed bulk modulus (K) of the glass according to the following semi-empirical formulas:

$$\alpha = \frac{\chi_1}{F}(F/K)^{m/4} \tag{1}$$

$$\alpha = \chi_2 \frac{[O]}{F}\ell^m \tag{2}$$

$$\alpha = \frac{\chi_1}{F}\left(F/10G_tV_t^2\right)^{m/4} \tag{3}$$

where x_1 and x_2 are two frequency dependent constants, whereas m is a positive power, its value depends upon the type of glass. During the last few years, the applicability of the first two semi-empirical formulas has been verified for a variety of phosphate, borate, silicate and tellurite glasses [33,34,36–38]. On the other hand, the semi-empirical relationship (3) has only been demonstrated for TiO_2-doped $CaO–Al_2O_3–B_2O_3$ and V_2O_5-Ag_2O-TeO_2 glass systems [35]. So, this semi-empirical relationship has not yet been established for a wide variety of inorganic oxide glasses. This fact was one of the motivating factors behind the present study.

Recently, phosphate-based glasses have attracted extensive research interest, due to their specific properties and correspondingly their

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potential suitability for technological and optical applications [38–41]. Therefore, the goal of the present work is to interpret and predict the composition dependence of ultrasonic properties in binary V_2O_5-P_2O_5 glasses, on the basis of Abd El-Moneim's semi-empirical formulas [33,35], bond compression model [19] and Makishima-Mackenzie's theory [20,21]. The most significant physical and compositional parameters, such as molar volume, excess molar volume, number of network bonds per unit volume, oxygen density, first-order stretching force constant, dissociation energy per unit volume and packing density of the glass were evaluated and correlated to elastic moduli and ultrasonic attenuation coefficient. Values of the theoretical elastic moduli have also been calculated and compared with the corresponding experimental ones.

2. Significant compositional parameters

The different significant compositional parameters of inorganic oxide glasses can be evaluated from their chemical composition as follows.

2.1. Molar volume

Molar volume (V_M) of multi-component glasses can be calculated from the following relation:

$$V_M = \sum_i x_i M_i/\rho \tag{4}$$

where x_i and M_i are the respective molar fraction and molecular weight of oxide component i, whereas ρ is the glass density.

2.2. Packing density and dissociation energy per unit volume

On the basis of Makishima-Mackenzie's theory [20,21], packing density (V_t) (defined as the ratio of minimum theoretical volume occupied by the ions to the effective volume of the glass) and dissociation energy per unit volume (or volume density of energy) (G_t) of multi-component oxide glasses can be expressed in terms of packing density of atoms and dissociation energy of the oxide constituents per unit volume according to the following relationships

$$V_t = \frac{\rho}{M}\sum_i x_i\, V_i \tag{5}$$

$$G_t = \sum_i G_i x_i \tag{6}$$

where V_i and G_i are the respective packing factor and dissociation energy per unit volume of oxide component i, whereas $M = \sum x_i M_i$ is the molecular weight of the glass. The packing factor and dissociation energy per unit volume can be calculated for an oxide A_yO_z from the following equations:

$$V_i = \frac{4}{3}\pi N_a\left(yR_A^3 + zR_O^3\right) \tag{7}$$

$$G_i = \frac{\rho_i}{M_i}U_i \tag{8}$$

where N_a is Avogadro's number, R_A and R_O are the respective ionic radius of metal and oxygen, whereas ρ_i and U_i are the density and dissociation energy per mole (molar dissociation energy) of the oxide i.

2.3. Average first-order stretching force constant and number of network bonds per unit volume

The average first-order stretching force constant of a multi-component oxide glass samples can be estimated from an equation reported by Higazy and Bridge [32] in the form

$$F = \frac{\sum_i x_i n_i f_i}{\sum_i x_i n_i} \tag{9}$$

where n_i is the number of network bonds per cation (coordination number of cation) in oxide component i with cation-anion bond length r_i and first-order stretching force constant $f_i = 17/r_i^3$. On the basis of the bond compression model [19], the number of network bonds per unit volume can be calculated, for of a multi-component oxide glass, using the following relation

$$n_b = \frac{N_a}{V_M}\sum_i x_i n_i \tag{10}$$

3. Analysis and discussion

Table 1 summarizes the data of room temperature density and ultrasonic properties of the investigated V_2O_5-P_2O_5 glasses. The applied data of bulk modulus and ultrasonic attenuation coefficient are those measured previously by Mukherjee et al. [4] at 8 MHz frequency using ultrasonic pulse-echo overlap method, whereas data of Young's modulus were taken from Ref. [5]. The accuracy of ultrasonic attenuation measurement is estimated to be about ±2%. The estimated values of molar volume are also listed in the same table. The increase of density with increasing V_2O_5 concentration can be attributed to the substitution of P atoms by heavier V atoms. Generally, it is expected that the molar volume and density should show opposite behavior to each other. In case of the present glasses, both the density and molar volume follow a linear increase with the substitution of P_2O_5 by V_2O_5 (see Table 1). These results indicate that the composition dependence of molar volume in these glasses is related to the type of structural units that form when V_2O_5 is incorporated into the glass structure rather than the constitution of the glass. Similar anomalous behavior between density and molar volume has also been reported previously for binary PbO-P_2O_5 [6] and ternary V_2O_5-Li_2O-B_2O_3 glasses [7]. However, the composition dependence of molar volume in the present V_2O_5-P_2O_5 glasses will be explained in Section 3.1.

Fig. 1 illustrates the compositional dependence of elastic moduli in binary V_2O_5-P_2O_5 glasses through the investigated composition range from 45 to 85 mol% V_2O_5. The figure shows clearly that, when P_2O_5 is substituted by V_2O_5 a decrease in both bulk modulus (K) and Young's modulus (E) is noted. The decrease of elastic moduli indicates a reduction in the rigidity (weakness) and loose packing of the glass network. Generally, it is expected that the elastic moduli and ultrasonic attenuation coefficient should show opposite behavior to each other. This is true in case of the studied V_2O_5-P_2O_5 glasses as shown in Table 1.

3.1. Structure of binary V_2O_5-P_2O_5 glasses

It is a well-known fact that, P_2O_5 is one of the glass forming oxides [19]. The structure of pure P_2O_5 glass consists of a 3-dimenstional network of three-fold corner-connected PO_4 tetrahedra, which are connected to each other through the P-O-P linkages [19]. The fourth corner is terminated with a P═O double bond. On the other hand, transition metal oxide V_2O_5 is classified a conditional glass former [4,8,42]. This oxide can enters the same network either as a network-modifier or as a network-former in V^{5+} valence state by formation of VO_5-groups or in V^{4+} valence state by formation of VO_4-groups, depending upon its concentration [4,8,42]. A review of literature indicates that many attempts have been made to explore the structural role of V_2O_5 in the network of phosphate glasses, using an X-ray photoelectrons spectroscopy (XPS) and magnetic susceptibility studies [43], neutron diffraction investigation [44], X-ray and neutron diffraction [45], IR spectra [46,47]