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Acoustic Debye Temperature of Ternary PbO–CuO–B2O3 Glasses

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***ABSTRACT* :** **Acoustic Debye temperature of the ternary borate glass system xPbO–(45-x)CuO– 55B2O3 was studied in the composition range x = 5 - 40 mol % by using ultrasonic pulse-echo technique. The composition dependence revealed broad humps at 20mol % PbO. Below 20mol%,all Pb+2 ions are considered to be entering the borate network as a glass modifier. This transforms the borate network from an open structure to a denser three-dimensional structure due to BO3 → BO4 conversion. The addition of PbO beyond 20 mol% results in the formation of PbO4 structural units and B–O–Pb linkages in addition to NBOs. This weakness the glass structure and decreases the acoustic Debye temperature. A correlation between acoustic Debye temperature and compositional parameters was achieved when the change in boron coordination numbers is taking into account. In Egypt, the shortage of freshwater resources and their pollution constitutes a growing concern. Due to the uncensored use of pesticides in the agricultural regions of Egypt, the contamination risks of ground water increase periodically in planting seasons. Therefore, the present work aims to monitor the occurrence of organochlorine pesticides (OCPs) residues and heavy metals in five ground water samples collected from agricultural area with long-term pesticide application history in Belbis region, El-Sharqia, Egypt. Water samples were processed using a solid-phase extraction technique and gas chromatograph equipped with mass spectrometry (GC-MS). Results revealed that, the concentrations of OCPs in groundwater are in the limits except only 0.65 μg/L of p,p'-DDT recorded in ground water at Hassan Bieh village location, Belbis region, El-Sharqia, Egypt. Levels of iron and manganese in (Elnoba and Awlad Mahnaa) ground water samples were found to be much higher than the limits of Egyptian quality standards. The other elements in this study were found in the limits. The turbidity in 3 site (Hassan Beih, Elnoba and Awlad Mahnaa) villages has high values (4.7, 28.4 and 4.4), respectively. TDS values in two sites (Hassan Beih and Awlad Mahnaa) villages showing values above the 1000 mg/L limit.**

KEYWORDS: Borate glasses; Acoustical Debye temperature; compositional parameters.

I.   INTRODUCTION

B2O3 is a glass former because of its high bond strength, small cation size, small heat of fusion, and the valence (=3) of B. The network of pure B2O3 glass is composed of corner-sharing BO3 triangles and most of these triangles are arranged into boroxol rings, that is, planar rings containing three boron atoms and three oxygen atoms (1-3). The addition of a modifier oxide (e. g., alkali oxide) to vitreous B2O3 causes a change in the co-ordination number of boron from three to four, which increases the connectivity and rigidity of the network. Up

to certain composition, some properties show a gradual change followed by a sudden change of trend starting from a definite point of structural inversion. This extreme behavior is known as borate anomaly (4). The occurrence of borate anomaly was found to be depends on the concentration and type of the added modifier. For example, the substitution of Na2O by Li2O in (50-x)Li2O–50B2O3–xNa2O glasses up to 15 mol% leads to a gradual increase in the fraction of four coordinated boron atoms (N_4) (3). Beyond 15 mol%, the addition of Na2O results in reconversion of BO4to BO3 units and loose structure due to the creation of NBOs.

Borate-based glasses are very interesting amorphous materials considering their specific structure and physical properties (5-8). The ultrasonic nondestructive pulse-echo technique plays a significant role in understanding the structural characteristics and studying mechanical properties of glasses as a function of composition. Previous studies (9-13) revealed that PbO shows an interesting behavior in the formation of lead silicate, lead borate and lead phosphate glasses. It acts both as a network modifier and as a network former depending upon its concentration (11, 13-15). Debye temperature is a useful parameter when investigating changes in structure and mechanical properties of glasses. It represents the temperature at which all modes of vibrations in a glass are excited and its increase implies an increase in the rigidity of the glass. The purpose of this study is to declare the structural role of PbO in xPbO–(45-x)CuO–55B2O3 glass system through a wide range of composition. The dependence of the acoustic Debye temperature on PbO concentration was studied. Correlations between acoustic Debye temperature and compositional parameters have also been investigated.

II. MATERIALS AND METHODS

2.1 Samples preparation

Investigated lead-copper-borate xPbO–(45-x)CuO–55B2O3 glasses, where x = 5, 10, 15, 20, 25, 30, 35 and 40mol%, were prepared by employing the melt quenching technique as described in (16).

2.2 Determination of the acoustic Debye temperature

The acoustic Debye temperature of each investigated glass sample was calculated from the measured ultrasonic velocity and density data according to the following standard relation (17):

Debye temperature
$$\theta_D = \frac{h}{B}\left[\frac{3\Psi N_a}{4\pi V_M}\right]^{\frac{1}{3}} V_m \tag{1}$$

Mean ultrasonic velocity
$$V_m = \left[\frac{1}{3}\left(\frac{1}{V_\ell^3} + \frac{2}{V_s^3}\right)\right]^{-\frac{1}{3}} \tag{2}$$

Where V_M is the molar volume of the glass, h is Planck's constant, B is Boltzmann's constant, Ψ is the number of atoms in the formula unit of the glass, N_a is Avogadro's number, whereas V_ℓ and V_ℓ are the respective longitudinal and shear ultrasonic velocities.

III. RESULTS AND DISCUSSION

Values of the acoustic Debye temperature, which have been determined from the data of ultrasonic velocities and molar volume for all investigated xPbO–(45-x)CuO–55B2O3 glass samples are list in Table 1. The applied data of molar volume and ultrasonic velocities are given in the same table. Fig. 1 illustrates the effect of PbO on the acoustic Debye temperature through the composition range 5 mol% ≤ x ≤ 40 mol%. As can be seen from this figure, the acoustic Debye temperature shows a broad hump around 20 mol % PbO that might due to some changes in the structure of the glass at that composition. Likewise ultrasonic velocity and elastic moduli, the increasing trend of the acoustic Debye temperature in the composition range 5 mol% ≤ PbO ≤ 20 mol % implies the structure of the borate network becomes more rigid and strength with the substitution of CuO by PbO content. On the other

hand, the decreasing trend in the composition range 20 mol % < PbO ≤ 40 mol % is attributed to the softening of glass structure. Kodama et al. (18) reported that BO3 structural units in binary alkali borate Li2O-B2O3 glasses are converted to BO4 structural unit only in the compositional range 0 < Li2O < 0.20 mol % and this conversion caused an increase in the velocity of sound and rigidity of the glass network. The acoustical Debye temperature of 30RO–30Al2O3–40B2O3 glasses, where R = Mg, Ca or Sr, have been analyzed quantitatively (17) by using the bond-compression and ring-deformation models (19). It has been found that the transformation of neutral borate triangles, BO3, into charged borate tetrahedral, BO4, as well as the change in the cross-linking density and atomic ring size, play an important role in determining the elastic moduli and Debye temperature.

Table 1: Glass composition, physical and Debye temperature 0f xPbO-(45-x)CuO-55B2O3 glasses.

X (mol %)	$V_{M\,(16)}$ (cm3/mol)	$V_{\ell\,(16)}$ (m/s)	$V_{s\,(16)}$ (m/s)	θ_D (°k)	$N_{4(16)}$	$V_{t\,(16)}$
5	17.31	4,446	2,295	384.77	0.445	0.7767
10	17.65	4,407	2,292	381.61	0.443	0.7705
15	17.93	4,397	2,488	409.47	0.453	0.7692
20	18.15	4,662	2,446	403.20	0.477	0.7726
25	18.59	4,408	2,382	388.72	0.500	0.7668
30	18.90	4,369	2,272	369.71	0.517	0.7656
35	19.25	4,022	2,206	355.43	0.506	0.7580
40	19.76	3,952	2,073	332.19	0.517	0.7485

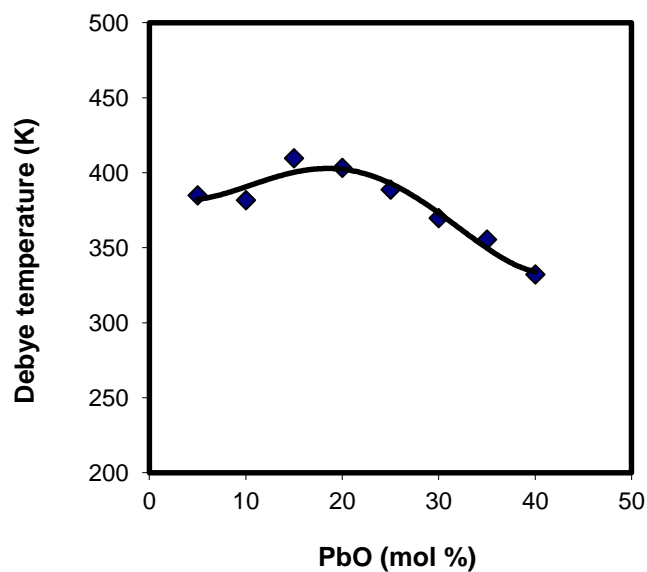*Fig. 1: Composition dependence of Debye temperature in ternary xPbO-(45-x) CuO-55B2O3 glasses.* The solid line is drawn as a guide to the eye.

The observed non-linear change in the acoustic Debye temperature of xPbO–(45-x)CuO–55B2O3 glasses can be explained on the basis of the structural consideration of the borate network as follows:

1. Our previous FTIR spectra of the same present glasses concluded that, below 20 mol % PbO, there is a growth in the concentration of BO4 tetrahedral units and expense of BO3units (BO3→ BO4 conversion).This results formation of tri-, tetra-, di-and penta-borate structural groups without NBOs. As a result, the fraction of four coordinated boron atoms (N4) increases, which in turns increases the acoustic Debye temperature with increasing PbO content. Beyond 20 mol % PbO, the fraction of four-coordinated boron atoms shows a slight change with the substitution of CuO by PbO. At the same time, the molar volume of the glass showed a higher rate of increase due to the formation of meta-borate, BØ2O-, pyro-borate, B2ØO4-4 and ortho-borate, BO3-3 units (Ø = bridging oxygen atom and O = non-bridging oxygen atom) (20). This decreases the network connectivity as evidenced by the decrease of ultrasonic velocities and Debye temperature.

2. The field strength of modified ions (ε = Z/ [Rc + Ro]) 2, where Z is the valence of cation, Rc is the ionic radius of cation and Ro is the ionic radius of oxygen) is one of the prominent factors in explaining changes in the elasticity of glasses. In compared to Cu2+ ions, Pb2+ ions have smaller field strength (21). Thus, the presence of Pb2+ ions with concentration greater than that of Cu2+ ion will weakness the glass structure and decrease its elasticity. This argument explains changes in the Debye temperature of xPbO–(45-x)CuO–55B2O3 glasses with PbO > 20 mol%.

The above discussion can be support by correlating the acoustic Debye temperature with the total packing density of the glass. The values of packing density for xPbO–(45-x)CuO–55B2O3 glasses, which have been calculated on the basis of Makishima and Mackenzie's theory (22) and after taking into account changes in boron coordination numbers, are given in Table 1. Fig.2 illustrates the relation between acoustic Debye temperature and total packing density in for xPbO–(45-x)CuO–55B2O3 glasses. As expected, the acoustic Debye temperature increases with the total packing density. The increasing trend implies that the total packing density is a significant parameter for explaining changes in the acoustic Debye temperature of borated-based glasses. The glass structure becomes more close-packed and strength with increasing Debye temperature. The fitted curve can be represented by the relation $\theta_D = 1449\,V_t^{5.045}$ with R2 = 0.75.
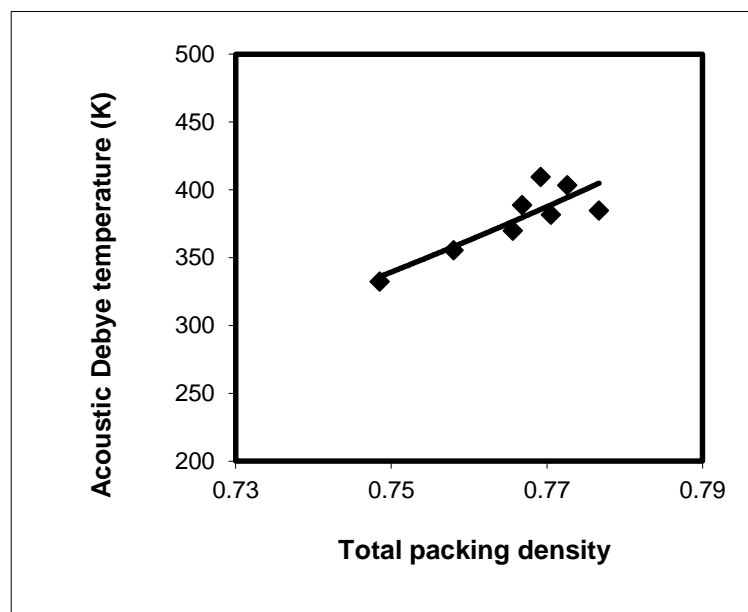
Fig. 2: Dependence of acoustic Debye temperature on total packing density *in ternary xPbO-(45-x) CuO-55B2O3 glasses.* The solid line represents the least-square fitting of the data

V –CONCLUION

The compositional dependence of acoustic Debye temperature has been studied in lead copper borate glasses with molar composition xPbO–(45-x)CuO–55B2O3 glasses (5 ≤ x ≥ 40mol %). Below 20 mol%, Pb+2 ions is considered to be enter the borate network as a network modifier and this changes the coordination number of boron from 3 to 4, which stiffness of the glass network greatly. Beyond 20 mol % PbO, the decrease of acoustic Debye temperature is attributed to the creation of NBOs. Correlation between acoustic Debye temperature and total packing density of the glass was achieved.

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