

**XRD, DTA AND DENSITY STUDIES OF LITHIUM
BORATE GLASSES CONTAINING COPPER**

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Abstract

Series of $(100-x)$ $\text{Li}_2\text{B}_4\text{O}_7 \cdot x\text{CuO}$ glass samples was studied with the help of XRD, DTA, glass forming ability (GFA), glass stability (GS) and density measurements. In the $x = 0-40$ range the mol% increased by step of 5 mol%. The XRD pattern of the investigated glass samples containing CuO up to 25 mol% showed that these glass samples are composed the glassy phase, and the partial crystallization occurred above it. The crystalline phase was identified as Cuprite Cu_2O . The calculations and the investigations used here enable us to evaluate the effect of copper addition to $\text{Li}_2\text{B}_4\text{O}_7$ glass samples on GFA and GS and to find a possible correlation between them. The substitution of copper oxide at the expense of $\text{Li}_2\text{B}_4\text{O}_7$ for the glass former causes the change in the values of T_g , T_x and T_i of the samples. The values of T_g for glass samples containing CuO up to 25 mol% are apparently lower than that in $\text{Li}_2\text{B}_4\text{O}_7$ samples free from CuO. This means that the substitution of CuO tends to extend the glass-working region and changes the oxides network. The increase in T_g above 25 mol% CuO shows that the structure of this interval concentration glass samples is progressively modified. Most of the CuO content enters as a modifier and the non-bridging oxygen decreases in the glasses network by increasing the copper oxide up to 25 mol%, which consolidate their structure and increase its density. Above 25 mol% CuO rearrangement in the network of the glass samples occurred and the CuO separates composing Cuprite Cu_2O phase which hence more compact structure is expected leading to higher density.

1. Introduction

The glass-forming ability (GFA) of a melt is evaluated in terms of the critical cooling rate for glass formation, which is the minimum cooling rate (R_c) necessary to keep the melt amorphous without precipitation of any crystals during solidification. The smaller R_c , the higher the GFA of a system should be. However, R_c is a parameter that is difficult to measure precisely. A great deal of effort has therefore been devoted to search for a simple and reliable gauge for quantifying GFA for the melt. As a result, many criteria have been proposed to reflect relative GFA on the basis of the characteristic temperatures measured by differential scanning calorimetry (DSC) or/and differential thermal analysis (DTA) [1–8].

The most extensively used are the reduced glass transition temperature, ($T_{rg}=T_g/T_m$ or $=T_g/T_l$, where T_g , T_m and T_l are the glass transition, the onset melting and the offset melting temperatures, respectively). Also the most extensively used is (ΔT_x), the width of the supercooled liquid ($\Delta T_x = T_x - T_g$ where T_x is the onset temperature of crystallization) where, the larger ΔT_x the higher the GFA, which means that the width of the supercooled liquid region can exist in a wide temperature range without crystallization and has a high resistance to the nucleation and growth of crystallization phases, leading to good GFA [1].

Some authors had found that the reduced glass transition temperature T_g/T_l shows a better correlation with GFA than that given by T_g/T_m [2–4]. Another parameter for GFA, the reduced crystallization temperature, $\gamma = T_x/(T_g + T_l)$, shows a stronger correlation with GFA than T_{rg} [5]. All these parameters are considered as empirical indicators of the GFA.

Glass stability, GS, accounts for the resistance of a glass towards devitrification upon reheating. Hrubý proposed that a parameter K_H , obtained by DTA or DSC, indicates glass stability against crystallization on heating [8]. Density was considered early as an important physical property in the field of glass science, especially where glass structure was concerned. The introduction of a definite amount of alkali into borate glasses consolidates their structure and increases its density [9]. Lithium borate glasses are of great interest because of their good ionic conductance properties [10]. In the present work, the effect of $x\text{CuO}$ on $(100-x)\text{Li}_2\text{B}_4\text{O}_7$ glass samples was studied using different techniques such as XRD, DTA and density measurements. Also the GFA and GS were calculated and discussed.

2. Experimental

A series of $\text{Li}_2\text{B}_4\text{O}_7$ CuO samples was prepared with different compositions. We started with the composition of 100 mol% $\text{Li}_2\text{B}_4\text{O}_7$, the concentration of copper oxide increased by step 5 mol% at the expense of $\text{Li}_2\text{B}_4\text{O}_7$. The used raw materials were all of chemically pure grade and were finely pulverized. The homogenous mixture was melted in platinum crucible in an electrically programmable heated furnace (type VAF 15 / 10 lenton thermal designs) equipped with an automatic temperature controller. The samples were melted at 1200 ± 20 °C for two hours with the heating rate 30 °C / min. The molted materials were stirred several times to ensure a complete homogeneity of the samples, then they were quenched in air and poured at room temperature. The samples were examined by using Philips Analytical X-Ray diffraction system, type PW 3710 based with Cu tube anode. Differential Thermal Analysis measurements (DTA) were carried out using a SHIMADZU DTA-50 ANALYZER. The measurements were carried out between 25 °C to 1000 °C (in N_2 gas using Al_2O_3 powder as a reference material, at the rate of 10 °C / min.). Glass density measurements were measured at room temperature using the standard Archimedes method, with toluene as the immersion fluid of stable density (0.866 g/cm³). The experimental error

was about $\pm 0.03 \text{ g/cm}^3$. The molar volume V_m was calculated from the molecular weight M and density ρ .

3. Results and Discussions

All the results are presented as a function of $x \text{ mol\% CuO}$ treating the investigated glass samples as pseudo-binary $(100-x) \text{ Li}_2\text{B}_4\text{O}_7 \cdot x \text{ CuO}$, where $x = 0, 5-40$ range $\text{mol\% CuO}$ increased by the step $5 \text{ mol\%}$ at the expense of $\text{Li}_2\text{B}_4\text{O}_7$. Figure 1 shows the XRD pattern of the investigated glass samples. Only a broad peak is observed for a glass sample free from CuO and for samples containing CuO up to $25 \text{ mol\%}$ indicating that these glass samples are composed of glassy phase. However, the glass samples containing $\geq 30 \text{ mol\% CuO}$ showed sharp diffraction peaks superimposed on a weak halo pattern, indicating partial crystallization occurred as shown in Fig. 1b. Therefore, the glass samples containing $\geq 30 \text{ mol\% CuO}$ are composed of the glassy phase and partially crystalline phases. The partially crystalline phase increases with increasing CuO content and identified as Cuprite Cu_2O [JCPDS-JCDD-5-667]. Figure 2 shows the DTA curves of $\text{Li}_2\text{B}_4\text{O}_7$ glass sample free from CuO and samples containing CuO up to $40 \text{ mol\%}$, respectively, at a heating rate of 10 K/min .

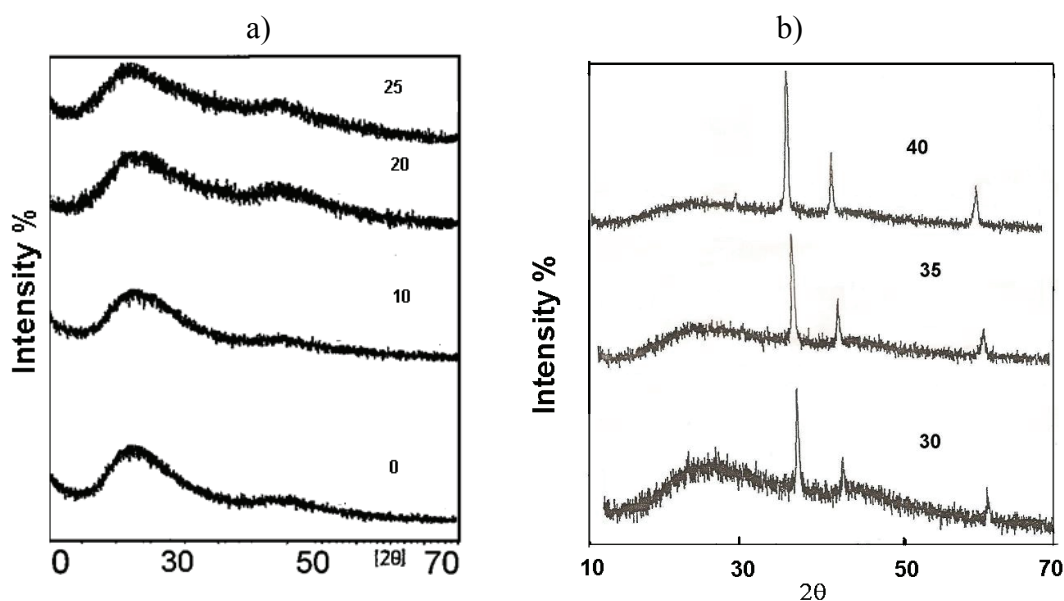


Fig. 1 a) XRD pattern of glass samples $\{(100-x) \text{ mol\% Li}_2\text{B}_4\text{O}_7 \cdot x \text{ mol\% CuO}\}$, where $x = 0, 5, 10, 15, 20, 25$ respectively. b) XRD pattern of glass samples $\{(100-x) \text{ mol\% Li}_2\text{B}_4\text{O}_7 \cdot x \text{ mol\% CuO}\}$, where $x = 30, 35$ and 40 respectively.

The effect of copper content on the thermal transition data for the investigated glass samples is shown in Fig. 3. It is observed from Fig. 3a that the glass transition temperatures T_g are shifted to lower temperatures with increasing CuO content up to $25 \text{ mol\%}$ and then shifted to higher temperatures. One exothermic peak follows the glass transition temperature indicating the stage of crystallization process. T_x is the onset temperature of the first crystallization event. It shows an increase with increasing CuO

content in the first three samples and then shifted to lower temperatures for samples above 10 mol% CuO as shown in Fig. 3b, where the higher T_x is the higher the thermal stability of the amorphous [5]. The exothermic peak is followed by two endothermic peaks for the first three samples, which show that the melting processes take place in two steps, while the other samples have one endothermic peak, T_m (onset melting temperature). The offset melting temperatures T_l are shifted gradually to lower temperatures by increasing CuO content up to 10 mol% CuO and then increased above it up to 25 mol% CuO and decreased at ≥ 30 mol% CuO as shown in Fig. 3c and followed by one or two exothermic events characteristic of crystallization processes as shown in Fig. 2b.

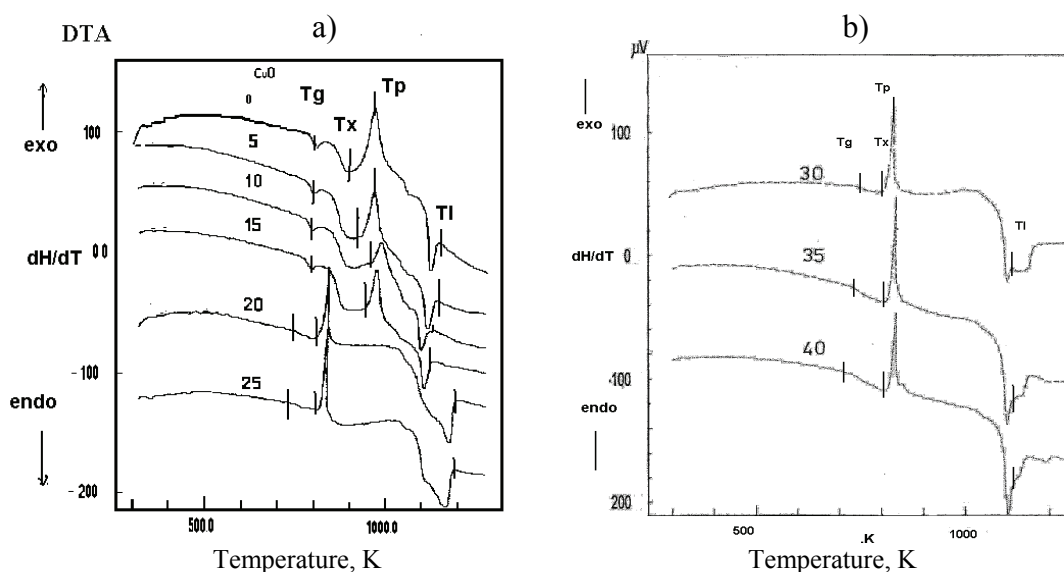


Fig. 2. a) DTA curves of glass samples $\{(100-x) \text{ mol\% Li}_2\text{B}_4\text{O}_7 \cdot x \text{ mol\% CuO}\}$, where $x = 0, 5, 10, 15, 20, 25$, respectively. b) DTA curves of glass samples $\{(100-x) \text{ mol\% Li}_2\text{B}_4\text{O}_7 \cdot x \text{ mol\% CuO}\}$, where $x = 30, 35$ and 40 respectively.

Thus, the substitution of copper oxide at the expense of $\text{Li}_2\text{B}_4\text{O}_7$ for the glass former causes the change in the values of T_g , T_x and T_l of the samples. This effect depends on: 1) density of covalent cross linkage, 2) oxygen density of the network and 3) number and strength of the cross-links between oxygen and the cations. In the case of the substitution by Cu at the expense of $\text{Li}_2\text{B}_4\text{O}_7$, we see that the values of T_g are apparently lower than that in $\text{Li}_2\text{B}_4\text{O}_7$ samples free from CuO. This means that the substitution of CuO tends to extend the glass-working region. The introduction of CuO into $\text{Li}_2\text{B}_4\text{O}_7$ samples changes the oxide network, since in the case of $\text{Li}_2\text{B}_4\text{O}_7$ glass the ratio of B_2O_3 and Li_2O is kept constant for all samples ($\text{Li} / \text{B} = 1/2$). Some of covalent B – O bonds in glass network would be expected to be replaced by weak ionic or covalent Cu – O bonds and also decrease the number of oxygen ion in network. This causes a decrease in the bond strength and a decrease in T_g values of the samples containing CuO up to 25 mol% [12]. The increase in T_g values above 25 mol% CuO reveals that the structure of this interval concentration glass samples is

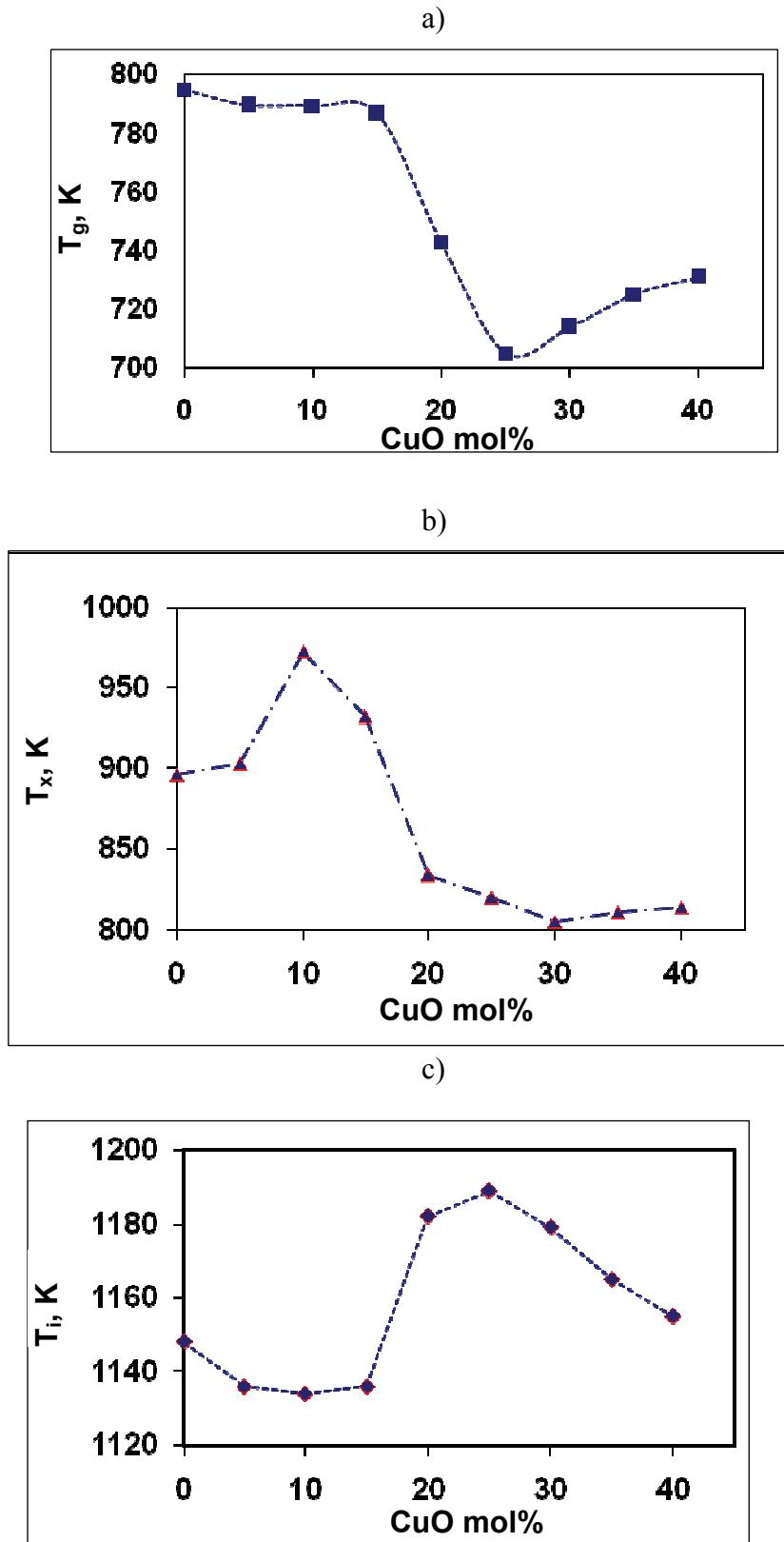


Fig. 3. The effect of the copper content on the thermal transition data for the investigated glass samples, where: a) the glass transition temperature, T_g vs. copper content; b) the onset crystallization temperature, T_x vs. CuO content; (c) the offset melting temperature, T_i vs. copper content.

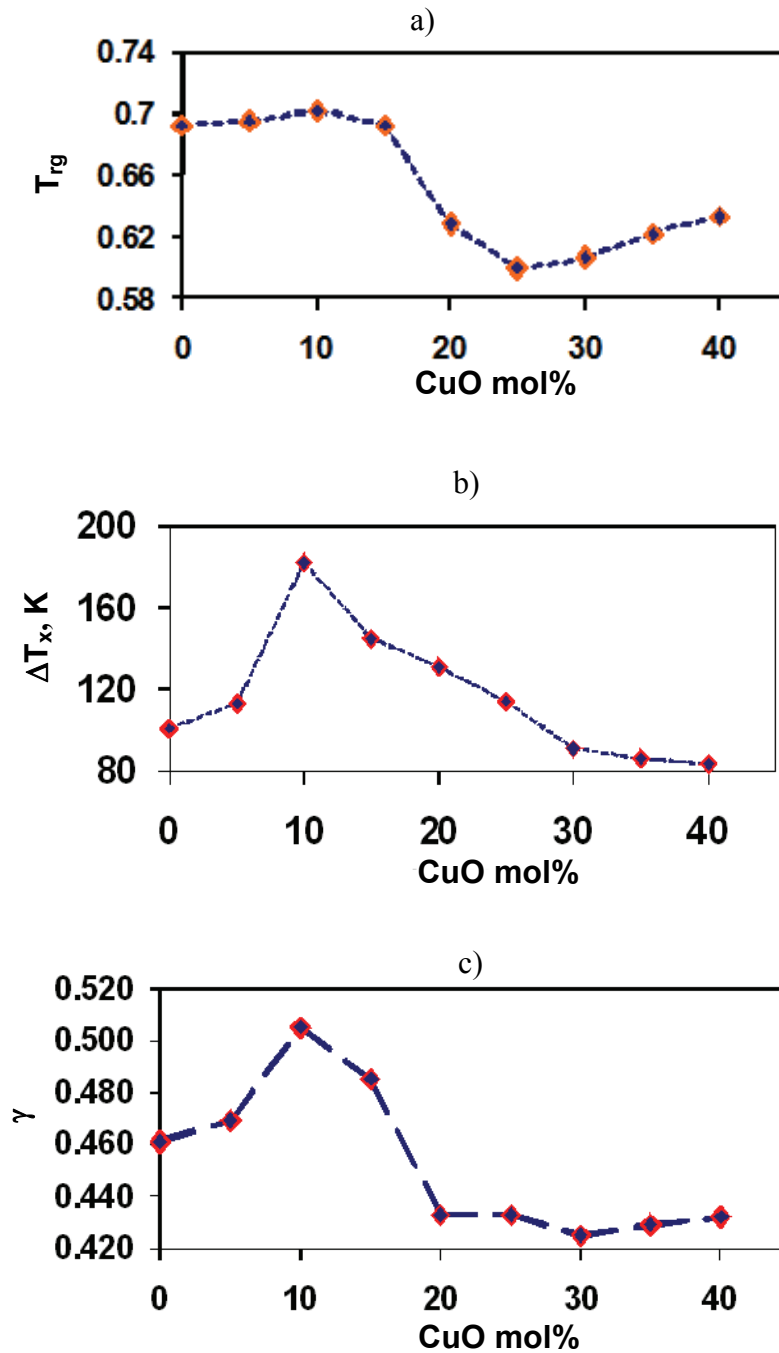


Fig. 4 a) the reduced glass transition temperature, T_{rg} vs. copper content; b) the GFA parameter ΔT_x vs. the copper content; c) the reduced crystallization temperature, γ vs. copper content.

progressively modified. It could be assumed that in this case CuO can be incorporated into the network resulting in the formation of B – O – Cu linkages with a covalent character, which yields a mixed network forming character, in accordance with the increase in T_g .

There are several parameters have been used to estimate the GFA of glasses: 1) the reduced glass transition temperature $T_{rg} = T_g / T_l$ [2–4, 13], which reflects the difficulty

of nucleation of crystallization phase during cooling from supercooled liquid. The calculated values of T_{rg} slightly increases by increasing the CuO content up to 10 mol% and then decreased with increasing CuO content up to 25 mol% and then increased at ≥ 30 mol% CuO as shown in Fig. 4a. So the reduced glass transition temperature T_{rg} has a higher value at 10 mol% CuO content glass sample indicates GFA and high thermal stability of the supercooled liquid region against crystallization [13]. Also the trend in the Fig. 4a indicates that the glass samples change to different states at ≥ 30 mol% CuO and this agrees with the results of XRD analysis. 2) supercooled liquid region ΔT_x , defined as $T_x - T_g$, is an indication of devitrification tendency of a glass when heated above T_g . Generally, the larger temperature interval ΔT_x , the higher the GFA [1]. The calculated values of ΔT_x increase with increasing CuO content up to 10 mol% CuO and then decrease as shown in Fig. 4b. As stated, the large values of ΔT_x imply that the supercooled liquid can exist in a wide temperature range without crystallization and in turns has a high resistance to the nucleation and growth of crystallization phases, leading to good GFA [14]. So, the results of ΔT_x for the investigated glass samples are a good indicator for easy glass forming for glass sample content up to 10 mol% CuO [13] leading to good GFA, while above 10 mol% CuO they could exist in a narrow temperature interval ($T_x - T_g$) range without crystallization and have a low resistance to the nucleation and growth of crystallization phases, leading to easy crystallization ability by increase in the CuO content. The comparatively values of the temperature interval ($T_x - T_g$) for the glass sample containing ≥ 30 mol% CuO reveal that there are not in a fully glassy state and also not in a fully crystalline state. Then the glass samples content up to 10 mol% CuO is composed of glassy phase with high resistance to the nucleation and growth of crystallization, above 10 mol% CuO are composed of glassy phase with decreasing resistance to the nucleation and growth of phases by increase the CuO content up to 25 mol% and above it a partial crystallization has occurred with CuO content. This is consistent with the results of XRD analysis.

3) $\gamma = T_x / (T_g + T_l)$, which is obtained by simple additive assumption of devitrification tendency of a glass and suppression of crystallization during solidification [5], it describes the GFA and the thermal stability. The calculated values of γ are increased by increasing the copper content up to 10 mol% CuO content and then decreased as shown in Fig. 4c. Hruby proposed that a parameter K_H obtained by DTA or DSC indicates glass stability against crystallization on heating [8,14]. This parameter is defined as $K_H = (T_x - T_g) / (T_m - T_x)$. The large value of K_H indicates the greater stability of the glass against devitrification. Critical cooling rates are normally rather difficult to measure; hence, it is important to assess GFA via other easily measured properties such as GS parameters [8,14]. Quantitative measurements of GS are formulated through the onset crystallization temperature observed in non-isothermal DTA measurements. Therefore the calculations of K_H , is made to investigate a possible correlation between GS and GFA for $Li_2B_4O_7$ containing CuO

from 0 to 40 mol% glass samples. The calculated values of the parameter K_H are shown in Fig. 5. It is observed that the values of K_H are shifted to higher values with increasing copper content up to 10 mol% and then decreased with increasing CuO content. The GFA parameters ΔT_x , γ and GS parameter K_H have the same trend with a significant decrease when a partial crystallization occurs. All of them assume a maximum at 10 mol% CuO which corresponds to the best GFA and GS. Then the values of K_H exhibit relatively better correlation with the GFA parameters ΔT_x and γ , while T_{rg} shows a poor relationship with the GFA of the investigated glass samples. Thus, the GS and the GFA are directly related. This result is compared with other literature [14] and exhibits relatively better correlation.

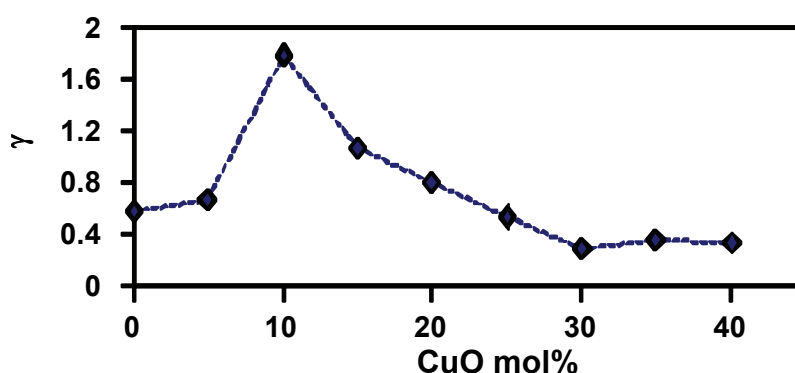


Fig. 5. The GS parameter K_H vs. the copper content.

Earlier it was stated that the density measurement is a very sensitive tool that can easily detect any structural changes in the glass network. The obtained values of the density were gradually increased as copper oxide content increased in the investigated glass samples up to 25 mol% CuO and then largely increased at ≥ 30 mol% CuO as shown in Fig. 6. It is obvious from the trend of the values shown in Fig. 6 that the glass samples changed their state to different states at $\text{CuO} \geq 30$ mol%. It can be supposed that some sort of rearrangement may take place in the network of glass samples containing $\text{CuO} \geq 30$ mol% [9]. The results of XRD and the calculated parameters above could confirm that these glass samples are still in amorphous state up to 25 mol% CuO, and there is a detectable change to partial crystallization at $\text{CuO} \geq 30$ mol%. Then, all tools had confirmed that the glass samples with ≥ 30 mol% CuO are partially crystallized. So the increase in density of the investigated glass samples up to 25 mol% CuO could be attributed to the differences in properties of both lithium tetraborate and copper oxide. Most of the copper enters as a modifier in the glass samples network and also the non-bridging oxygen decreases in the glasses network by increasing the copper oxide up to 25 mol%, which consolidate their structure and increase its density [9]. The investigated glass samples with ≥ 30 mol% CuO composed of glassy phase and partially crystalline phase show a larger increase in their density. This may be caused by the rearrangement of CuO in the network of the glass

samples when CuO separates composing Cuprite Cu_2O phase; hence, a more compact structure is expected leading to higher density.

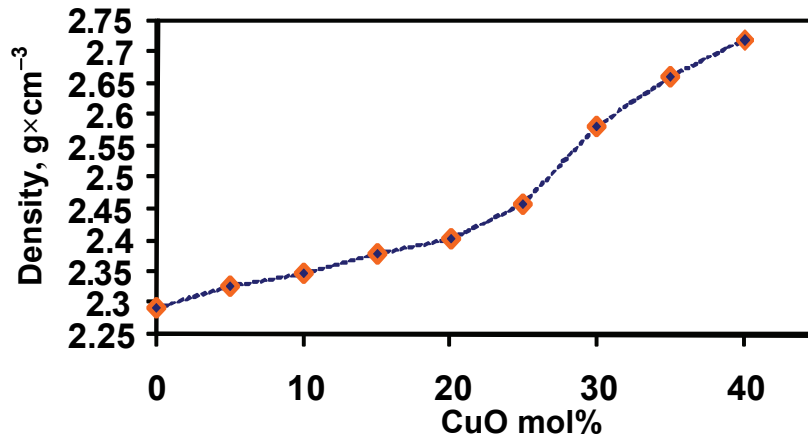


Fig. 6 The density vs. the copper content.

The glass molar volume V_m , was calculated; it decreases with increasing CuO content as shown in Fig. 7. The steepest change in the molar volume already occurs when the concentration of CuO increases up to 25 mol% and above it decreases faster as clear in Fig 7. This could be explained by considering the formation B–O – B linkages [15] with strong covalent B and Cu oxygen bond. Thus, the substitution of a longer ionic Li – O bond for a shorter covalent bond leads to the close structure of the glasses [16].

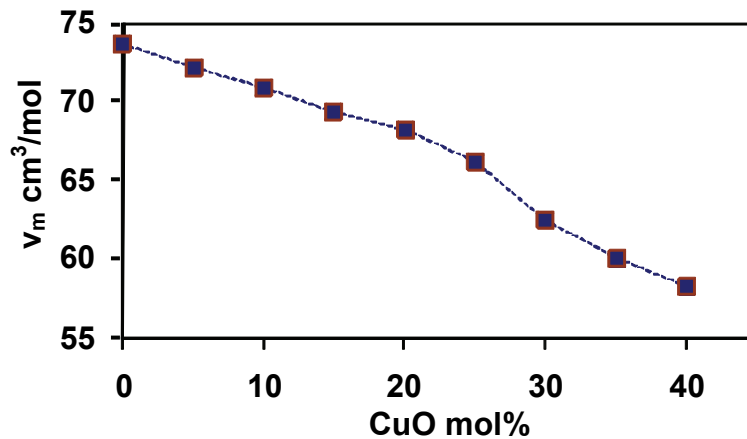


Fig. 7 The molar volume vs. the copper content.

4. Conclusions

According to the obtained results and the supposed discussion, it can be concluded that the XRD pattern of the investigated glass samples containing CuO up to 25 mol% showed that these glass samples are composed of glassy phase. However, the glass samples containing ≥ 30 mol% CuO are composed of glassy phase and partially crystalline phases. The crystalline phase is identified as Cuprite Cu_2O . GFA parameters

ΔT_x and γ follow the same trend with the GS parameter K_H . All of them confirm the XRD results and assume a maximum at 10 mol% CuO which corresponds to the best GFA and GS. The GS and GFA are directly related. The obtained values of the density were gradually increased as the copper oxide content increased in the investigated glass samples up to 25 mol% CuO and then largely increased at $\text{CuO} \geq 30$ mol%. The glass molar volume V_m was calculated; it decreases with increasing CuO content with a significant decrease when the partial crystallization occurs.

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