Effect of barium addition and plasma nitriding treatment on chemical and physical properties of Al, Pb borate glass system as a developed radiation shield.

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Abstract. The effect of the BaO addition of to aluminum, lead borate in a series of (BaO)x (B2O3)60-x (Al2O3)10 (Li2O)10 (PbO)20 glasses where x = 0 to 50 weight% have been studied through their shielding, mechanical, thermal and chemical properties. The physical parameters such as molar volume (Vm), density (ρ), and oxygen packing density (OPD) were evaluated and discussed. Moreover, the thermal stability of the investigated system increases with BaO content. The present study proved that each of the plasma nitriding treatments of the samples and/or increasing Ba content greatly improved their ability to resist scratching and corrosion. Therefore, the obtained results are candidates for the present glass system to be effectively used as a protective shield against nuclear radiations in many advanced domains.

1. Introduction
The development of special radiation protection materials made from glasses, especially optically clear glasses, has gained considerable attention recently rather than known standard shielding materials [1]. B2O3 is one of the most typical glass network formers. The composite structure of the glass chemical element is assumed to include the main boroxol rings and a few BO3 triangles with B-O-B linkages[2]. The application of lead borate glasses in many electronic goods fields is considered to be of technological importance for having low melting temperatures[3]. This can be the result of the upper polarization of the associated particles, and the low melting temperature of the material. Widely, low-melting glasses are used to reduce the temperature of sintering and improve the constant thermal growth in the field of electrical appliances[3]. BaO is known as a modifier, which is an alkali earth oxide that converts several symmetric boron to tetrahedral coordination, as well as metal element cations that occupy opening positions within the glass network. In general, there are various researches were carried out to improve the physical properties and the chemical durability of oxide glasses by adding different types of metal oxides to the glass structure. For example, lead oxide (PbO) is a heavy metal oxide. Combining Pb2+ ions in the borate glasses to improve the chemical stability and moisture resistance by forming B-O-Pb bonds, also by creating non-bridging oxygens (NBOs) atoms by incorporating lead oxide into the glass host[4]. PbO plays a dual role, PbO2 as a modifier in structural units and PbO4 as a glass former in structural units[5, 6]. Previous studies have referred to the possibility of using lead (Pb) and barium (Ba) in radiation protection applications[7-11]. The attenuation coefficient is an indicator of the radiation absorption of the nuclear material. The mass attenuation constant μm is a very important and necessary tool for determining different shielding parameters.
The surface of the glass is one amongst the most necessary factors that control chemical, physical, and photoelectric properties. Different surface treatment techniques are used for its improvement and one amongst the advanced techniques is surface bonding activated by reactive nitrogen ions etching plasma. The nitrogen ions etching plasma modifies the mechanical properties [12]. The objective of this work is to determine experimentally the mass attenuation constants (μ/ρ) of (BaO)x (B2O3)60-x (Al2O3)10 (Li2O)10 (PbO)20 glass systems where x = 0 to 50 weight% within the energy range from 662 to 1333 keV. The corresponding theoretical values are obtained using the computer WinXCom code [9, 10] for comparison. In addition, the electron and atomic cross sections, the effective atomic number and the neutron mass removal cross-sections ∑R/ρ (cm² g⁻¹) are identified. Furthermore, the present study was expanded to include the effect of nitrogen dense plasma focus (NDPF) on hardness and corrosion rate of the investigated glass systems to illustrate its capability as a proper radiation shield.

2. Materials and methods.
Glass samples BaPbBGs of composition (BaO)x (B2O3)60-x (Al2O3)10 (Li2O)10 (PbO)20 where x = 0 to 50 weight% were prepared from pure chemicals during a powder kind form by the melt quenching technique within the electric furnace at 1100 °C and the melting was continuing for 120 minutes together with rotating the melts at intervals to plug complete combination and homogeneity of the glasses. The melts were solidified into slightly warm stainless-steel molds of specified dimensions and the collected samples were directly transferred to associate an annealing muffle regulated at 350 °C. The annealing muffle was switched off after 1/2 hour and the muffle was left to reach room temperature. The prepared glass samples were investigated by X-ray diffraction to substantiate the amorphous state of the samples.

The density of glass samples at room temperature was measured by employing a sensitive balance with pure toluene.

A Vicker’s diamond indentor was employed in a customary microhardness tester (Leco AMH one hundred, USA) for specimen indentation. A load of three hundred grams applied for fifteen seconds to create indentations in specimens of glasses. Each sample was subjected to eight indentations at every measurement. Therefore, errors in the measured values such as the quality deviation area unit were precisely adopted. The diagonal length impressions were measured and also the hardness H was calculated consistent with a customary formula: H = 1.854 P/d² [13] where P is the indentation load, and d is the diagonal length impression. The microhardness was measured for the polished glass samples underneath investigation within plates of 2.5 mm thickness.

Chemical Durability of the glasses was used to measure the weight loss of samples immersed in distilled H2O and in CuSO4. To conduct these measurements, and to measure shielding properties, the samples were prepared in circle shape of diameter approximately has 2 cm long. The samples were polished exploiting assail papers and cleaned with acetone. The samples were dried and weighted before suspending them in the fifty ml CuSO4 solution while the rest was suspended in distilled H2O. The beaker was placed in an oven at 90°C. The specimens were removed, rinsed with a solution, dried, and weighted at the top of zero, fourteen and thirty days. Therefore, the measured weight loss (Δw) was simply obtained [13].

The dense plasma focus (DPF) was used to generate an ion beam which has a kinetic energy ranged from 400 to 500 keV and its lifetime was about 200 ns. The glass sample is put in a plasma chamber with nitrogen gas pressure 2 mbar at 6 cm from the plasma focus (ion beam source). The number of shots was 10 and the charging voltage was 12 kV.

Differential scanning calorimetry (DSC) measurements were allotted between room temperature and 650 °C in nitrogen gas using Al2O3 powder as a reference material with a slip-up estimation of (1°C) employing a sample weight of 10 mgm under flowing (50 mL/min) with a heating rate of 10°C/min.

60Co and 137Cs (10μCi) point sources were used to excite the targets. Gamma-ray intensity was measured using NaI (Tl) 2x2 scintillation detector. The samples were placed between the γ-ray...
supply and the detector. The detector absorbs a thin beam of γ-rays passing through the sample. To attenuate the impact of small-angle scattering within the target transmitted gamma rays were additionally collimated as shown in figure 1. The measurements were repeated five times to reduce all the associated errors.

![Figure 1. Experimental setup to determine the mass attenuation coefficients.](image)

3. Results and discussion.

3.1- Density and molar volume:

The practical values of the density and the molar volume for BaPbBGs are shown in figure 2. From the figure, the density of the glass samples increases with the rise of BaO content, but there is a high rise in the molar volume with BaO entry in the glass network followed by a reduction at higher Ba concentrations. However, the rate of change in molecular weight with 10% of barium in the network is bigger than the speed of modification in density as the structure of glasses changes. The same situation was observed for other glass composition [14]. O packing density (OPD) (g atm/l), was calculated exploiting the relation OPD = n (ρ/m), where n is the no. of oxygen atoms per formula unit and are presented in figure 2. The variation of O packing density within the composition of BaO as shown in figure 3 gives a further evidence for the conformability of the present glass system as its density increases, whereas O packing density decreases with the increase of BaO content.
3.2 Shielding properties.

The mass attenuation constants of the BaPbBGs were obtained by means of the mixture rule [15] using the following formula:

$$\mu/\rho = \sum w_i (\mu/\rho)_i$$  \hspace{1cm} (1)

where $w_i$ and $(\mu/\rho)_i$ were the fractional weight and the total mass attenuation constant of the $i$th constituent within the mixture respectively. The photon attenuation coefficients ($\mu$) of the samples...
were measured from the slope of attenuation curves at the photon energies of 662, 1173, and 1333 keV emitted from $^{137}$Cs and $^{60}$Co γ-ray sources, respectively. The variation of $\mu/\rho$ values for the prepared Al, lead borate glasses doped with BaO content within the energy range 662 to 1333 keV is conferred in Fig. 4. Figure 4 shows that $\mu/\rho$ values increase with increasing BaO content at low photon energies and reduce with the rise in photon energy. There is also an honest agreement between experimental values of mass attenuation constants with the corresponding theoretical values (WIN XCOM) [9]. This variation of $\mu/\rho$ can be explained by the photon energy emitted clearly on the premise of the various interactive processes (photoelectric process, Compton dispersion and pair production). In the low-energy zone, the photoelectric reaction is predominant, depending on the atomic number $Z^{4-5}$. Because of this dependence on the atomic number, maximum values were observed for $\mu/\rho$ within the low energy zone. Within the higher energy zone, Compton dispersion, that changes linearly with the atomic number is the main interaction. Therefore, $\mu/\rho$ values for all glass systems are nearly identical at the higher energies[4]. For better material as a radiation shield, higher $\mu/\rho$ values are desired. Hence, glass containing a large concentration of BaO is a superior shield to block the γ-rays.

![Figure 4. Mass attenuation coefficients of BaPbBGs as a function in BaO content in various photon energies](image-url)
Figure 5. The free path average (\( \lambda \)) of BaPbBGs as a function of BaO content at different photon energies.

The MFP represents the average distance traveled by particle motion between two consecutive collisions with other molecules. Figure 5 shows the dependence of the MFP values on totally different BaO concentrations in the energy range from 662 to 1333 keV. It is clear that MFP values are dropping with the increase of BaO concentration, indicating improved shielding efficiency of BaPbBGs. In light of these results, we tend to conclude that the present investigated glass containing an appropriate amount of barium content could be considered an effective gamma ray shield.

Fig. 6: Dependence of the effective atomic number for all BaPbBGs on different BaO concentrations
The BaPbBGs consists of different elements that give rise to an effective atomic number \((Z_{\text{eff}})\). It is used in many applications such as engineering applications, gamma beam attenuation, shielding purposes and many other fields of scientific applications. The effective number \((Z_{\text{eff}})\) of any composite materials is calculated according to the following equation
\[
Z_{\text{eff}} = \frac{\sigma_{t,a}}{\sigma_{t,el}} \quad (2)
\]
Where \(\sigma_{t,a}\) and \(\sigma_{t,el}\) are the full atomic crosswise and total electronic crosswise respectively. This number is related to a number of other characterizations of the composite material and is dependent upon the incident energy of gamma photons[18].

Figure 6 shows the behavior of the experimental \(Z_{\text{eff}}\) as a function of BaO content at different gamma energies compared with the corresponding theoretical values. It is observed from figure 6 that \(Z_{\text{eff}}\) values by which gamma-rays interact with BaPbBGs are different for different interaction processes and there is an increase in the \(Z_{\text{eff}}\) with the increase in the BaO content in BaPbBGs at low energy because of the higher cross-sectional values of both the photoelectric effect and Compton scattering. Hence, higher values of \(Z_{\text{eff}}\) at low energy are certainly accompanied with higher gamma-rays attenuation values. The actual physical removal of the fast neutrons \((\Sigma R)\) of BaPbBGs is delineated by a parameter known as the "removal cross-section", indicated by \(\Sigma R\) (cm\(^{-1}\)). The removal crosswise presents the likelihood that a quick or fission-energetic nucleon undergoes a primary collision that removes it from the cluster of penetrating un-collided neutrons[19, 20]. The removal cross-section for compounds could also be calculated from the worth of \(\Sigma R\) or \(\Sigma R/\rho\) for different elements within the compounds or mixtures by the following final formula;
\[
\Sigma R_i = \sum \rho_i (\Sigma R/\rho)_i \quad (3)
\]
where \(\rho_i\) and \(\Sigma R/\rho_i\) are the partial density of that glass and mass removal crosswise of the ith constituent, respectively.

Figure 7 Shows the mass removal crosswise \((\Sigma R)C\) as a function of BaO concentration. The calculated values of \((\Sigma R)C\) prove that the Ba free sample has the larger removal crosswise. It is well known that B\(_2\)O\(_3\) is much better than BaO in the absorption of neutrons. Therefore, the addition of BaO on the expense of B\(_2\)O\(_3\) reduces the values of the removal crosswise of those glasses. These results go parallel with the evidently expected decrease of thermal neutron cross-section values \(\sigma_{th}\) associated with the rise of BaO content and also the consequent decrease in the boron content \([\sigma_{th}(B) = 760\text{ barn}\) and \(\sigma_{th}(Ba) = 1.3\text{ barn}\).\] So, the problem here is how to compromise the concentrations of barium and boron oxides inside the glass matrix to have the proper shield for both neutrons and gamma radiations. The data displayed in figures 4 – 7 prove that the glass matrix containing only 10% BaO is the preferable one in this regard. Additionally, the present results recommend the produced glass matrix containing 10% BaO to be used successfully in the attenuation of neutrons and the associated gamma-rays emitted from the neutron source and that produced as a result of the neutron interactions with the glass matrix shielding material. As shown in figures 4 and 5 a very small change in gamma-ray mass attenuation coefficient after 10% BaO content is observed. Moreover, the data displayed in figure 7 clearly indicate that there is a significant rapid decrease in the removal neutron cross-section values after 10% BaO content. These results confirm the selection of the glass matrix containing 10% BaO to be the proper radiation shield.
3.3. Micro-hardness Measurements before and after Plasma Nitriding Treatments.

The focus dependence of the microhardness for the BaPbBGs on BaO contents are plotted in Fig. 8. As shown in this figure, the microhardness increases with the rise of BaO content. It is well-known antecedently that the microhardness of the glass mainly depends on the strength of the chemical bonds formed within the vitreous glass, and that the microhardness is associated with the hole theory[21].

The dense plasma focus (DPF) may be a supply of periodical radiation during which the current is born-again to plasma energy, leading to fugacious densities, (100 ns) dense (1025–1026 m$^{-3}$) and heat (1–2 keV) plasma. The nitrogen particle beams generated by the plasma column cause an enhanced change in the surface material[22] due to its broad characteristic of the energy spectrum (few keV to few MeV). These chemicals active ions interact with atoms emitted from the target material and form a thin nitride layer[22].

From Figure 8, it is obviously observed that the microhardness of the plasma treated glass is much higher than those attributed to the untreated original values. This is because the active ions have reached the glass substrate and transferred enough energy at a rapid rate to the substrate, that could achieve a high temperature rapidly, leading to local melting and evaporation. The explanation for the increase in the hardness of the samples is attributed to two totally different processes[23-24];

1st direct implantation of active nitrogen ions within the glass disc wherever these active ions will be incorporated into the glass grid and ions resulting from deformation of joints and distortions in the network structure,

2nd the reaction of nitrogen ions in the background with evaporative glass that can be re-deposited on the substrate surface thanks to the rear scattering of the fabric discharged by the comparatively high filling gas[23].
3.4. Weight loss measurements before and after Plasma Nitriding Treatments in different solutions. The corrosion of BaPbBG performance was tested at 90 °C before and after plasma treatment in water and concentrated CuSO₄ solution.

The experimental results indicated that weight loss may vary depending on the type of solution used and the composition of glass through BaO content. The results also indicated that there is an ability for these samples to strengthen the biographical structure and that the weight loss of corrosion varies with the nature of the solution. The highest corrosion was found in the BaO free sample while introducing at least 10% (wt %) BaO in the glass matrix causes a reduction in the corrosion value. Also, the corrosion rate in water for the glass sample is higher than the corresponding rate in the copper sulfate solution as shown in figures 9 and 10. So, the addition of BaO to that glass produces the greatest durability improvement. Moreover, Nitrided Plasma-treated samples have also significant improvement in their performance in either water or copper sulfate with respect to corrosion resistance or weight loss. This is mainly attributed to the formation of a passive protective layer on the samples that adds to them advantageous specifications such as strong bearing pressure and corrosion resistance that promote the use of this glass as a protective radiation shield in different nuclear applications. Also, figures 9 and 10 clearly show that the change in the weight loss for BaO concentrations more than 10% BaO is relatively minor which gives a further support for the glass system containing 10% BaO content as an optimum shielding material for both neutrons and gamma radiations.
Figure 9. The dependence of weight loss on the relative BaO content for BaPbBGs after 14 days.

Figure 10. The dependence of weight loss on the relative BaO content for BaPbBGs after 30 days.

3.5. Thermal behavior for BaPbBGs.
Thermal behavior of glasses was examined using differential scanning calorimetry analyses (DSC). The thermal scanning study of substances is of interest because it supplied précised information about thermal properties of such materials as well as some structural or phase transformations. DSC is used to determine the glass transition temperature ($T_g$), and the first crystalline
temperature (Tc). The value of glass stability against crystallization, ΔT, was simply calculated because the temperature distinction between glass transition onset and also the initial heat-releasing peak onset temperatures (∆T = Tc - Tg).

Figure 11 shows a DSC thermo-gram for a typical BaPbBGs system. The glass transition temperatures (Tg) are determined from DSC thermocouple for all the specimens in fig. 12 with a possible error of ±1 °C. The variation of Tg and characteristic temperatures with the composition of BaO is shown in Fig. 12. This figure exhibits the change in the characteristic temperatures (Tg and Tx) of BaPbBGs system. Tg shows approximately a gradual decrease.

Thermal stability of glasses is mainly due to the glass structure and thermally stable glasses have a closely packed structure. In contrary, the thermally unstable glass structure has a loose package [25]. Thermal stability is very important because of the incorporation of heat-generating wastes and/or high temperatures in the ground. If the glass has low thermal stability, the warehouses can cause the crystallization of the glass, which in turn leads to volume changes, thereby weakening the chemical durability and mechanical performance of the waste form. The glass stability, as shown in figure 12, increases with the rise within the BaO content. Consequently, the homogeneity of glass is to great extent expected to be increased.

Figure 11. DSC thermo-gram of BaPbB glass sample.
4. Conclusion

The results of the present work showed that the glass system (BaO)x (B2O3)60-x (Al2O3)10 (Li2O)10 (PbO)20 where (0 ≤ x ≤40 weight units %) has the capability to be proper gamma ray radiation shield as the BaO content increases especially at low energies. In contrary, the neutron attenuation coefficients decrease with increasing BaO content on the expense of boron. The obtained results illustrate that the strength of with-stand shocks, in addition, to the high heat and corrosion resistances are improved after plasma nitriding treatment. The insignificant change in the mass attenuation coefficient values and the rapid decrease in the removal cross-section values for glass samples having Ba concentrations more than 10% strongly support the superiority of the glass matrix having 10% Ba content among the other concentrations as a shielding material for both neutron and gamma radiations. Furthermore, the transparent behavior of the glass system achieved in the visible area and the good corrosion resistance results support our choice for the glass matrix having 10% Ba concentration as a nuclear radiation shield.

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