Ta$_2$O$_5$ Nanocrystals Strengthened Mechanical, Magnetic, and Radiation Shielding Properties of Heavy Metal Oxide Glass

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Abstract: In this study, for the first time, diamagnetic $\text{Ta}^{5+}$ ions and Ta$_2$O$_5$ nanocrystals were utilized to enhance the structural, mechanical, magnetic, and radiation shielding of heavy metal oxide glasses. Transparent Ta$_2$O$_5$ nanocrystal-doped heavy metal oxide glasses were obtained, and the embedded Ta$_2$O$_5$ nanocrystals had sizes ranging from 20 to 30 nm. The structural analysis of the Ta$_2$O$_5$ nanocrystal displays the transformation from hexagonal to orthorhombic Ta$_2$O$_5$. Structures of doped glasses were studied through X-ray diffraction and infrared and Raman spectra, which reveal that Ta$_2$O$_5$ exists in highly doped glass as TaO$_4$ octahedral units, acting as a network modifier. Ta$^{5+}$ ions strengthened the network connectivity of 1–5% Ta$_2$O$_5$-doped glasses, but Ta$^{5+}$ acted as a network modifier in a 10% doped sample and changed the frame coordination units of the glass. All Ta$_2$O$_5$-doped glasses exhibited improved Vicker’s hardness, magnetization (9.53 × 10$^{-6}$ emu/mol), and radiation shielding behaviors (RPE$\%$ = 96–98.8%, MAC = 32.012 cm$^2$/g, MFP = 5.02 cm, HVL = 0.0035–3.322 cm, and $Z_{eff}$ = 30.5) due to the increase in density and polarizability of the Ta$_2$O$_5$ nanocrystals.

Keywords: Ta$_2$O$_5$; mechanical property; radiation shielding; heavy metal oxide glass

1. Introduction

Transition metal oxides have been widely incorporated in vitreous materials due to optical changes and property enhancements to vitreous networks. In addition, transition metal oxides also strongly increase the chemical and thermal stabilities of glass formers because of their intermediary behavior related to a high coordination number of the metallic ions, resulting in higher connectivity of the glass network [1]. Among transition metal oxides, Tantalum oxide (Ta$_2$O$_5$) is an important tunable band gap and high-$\kappa$ (>20) dielectric material with interesting structural and functional properties [2]. Ta$^{5+}$ ions, with an empty $d$ shell ($d^0$ ions) having completely occupied the outermost electronic shell, can contribute to the diamagnetic character [3]. In addition, Ta$_2$O$_5$ has a high density, large refractive index, and a temperature-dependent structure; these features allow it to have potential applications in mechanical stability [4,5] and radiation shielding [6] applications. However, except for several Ta$_2$O$_5$ thin films, Ta$_2$O$_5$ has been less investigated due to its lower solubility in classical glass formers, as well as its high melting temperature (1825 °C). The studies of Ta$_2$O$_5$ are limited to several Ta$_2$O$_5$-doped silicate [7], phosphate [8–10], germinate [11], and tellurite [12] glasses for coating, photovoltaic, crystalization, and dielectric studies. Rare Ta$_2$O$_5$-doped heavy metal oxide glasses are reported, except recently published Bi$_2$O$_3$–TeO$_2$–ZnO glasses [12] and ZnO–Ta$_2$O$_5$–TeO$_2$ [8] by the Gokhan Kilic group.

Usually, transition metal ions act as glass network modifiers in glasses and provide a higher coordination number [13]. However, Ta$_2$O$_5$ is known as a conditional and poor glass “network-former”, compared with silica and phosphorus pentoxide. Ta$_2$O$_5$ is an
intriguing material because it is a “modifier” oxide composed of high field-strength cations, which has not been melt-quenched to form glass but is typically formed by ion beam sputtering [8]. At a lower content, it acts as a glass former, which increases the network connectivity with higher rigidity, resulting in a higher glass transition temperature and larger thermal stability against devitrification in phosphate glass [9] and 93GeO2–6Ta2O5–Bi2O3 glass [11]. Ta2O5 has been found to be a modifier, in most cases, at a higher content, which exists as TaO6 units [13,14]. In this case, the empty or unfilled d-orbital (outer electronic configuration 5d6s0) of Ta5+ ions strongly contribute to the large ionic refraction (23.4) and large refractive index and polarizability [15]. These features are attractive for magnetic properties.

Recently, the radiation shielding property of telluride glasses [16–20] and polymer [21] has generated much interesting research due to the introduction of highly dense and polarizable oxides, such as Ag2O, TeO2, Sb2O3, and so forth. Ta2O5 is a high density (8.2 g/cm3) material; the high density of Ta2O5-doped glass originated from the large packing effect of Ta in glass matrix [22] since the energy loss per traveled distance of gamma rays and charged ionizing particles (electrons, protons, alpha particles, ions) is proportional to electron density in the matter. Therefore, Ta2O5-doped transparent glasses with high densities are attractive in radiation shielding and a protective application in nuclear energy production and medicine [23,24]. Primarily, gamma radiation and X-rays emitted from the nuclear reactors with an elevated frequency are lethal since the interaction of ionizing radiation with materials requires dense elements with high atomic numbers, lower relaxation lengths, and lower half-value layers to be good radiation shielding materials [23]. Thus, glass components that have heavy metal oxides (e.g., PbO, Bi2O3) show excellent shielding properties under gamma and X-ray [25]. Two Ta2O5-doped tellurides [8,12] glasses and one Ta2O5-doped borate glass [22] were reported recently for radiation shielding study. However, Ta2O5-doped heavy metal oxide glass have still not been investigated, but it is expected to be the most ideal candidate for shielding applications.

The influence of the high polarizability and high refractive index (n = 2.18 at 550 nm) of Ta2O5 is not clear in terms of the radiation shielding of glass. Similar to Ta2O5, PbO plays dual roles in glass-forming as well. The network former Pb2+ ions impart a three-dimensional spatial network character to the glass. In fact, the easily polarizable valence shell of the Pb2+ ion strongly interacts with the highly polarizable O2− ion, giving rise to a rather covalent Pb–O bond [26]. The highly polarizable ions (Bi3+, Pb2+), from modifier Bi2O3 to glass, can prevent melt crystallization by the asymmetry structure resulting from oxygen polyhedra. Bi2O3 is found to exist as BiO3 pyramidal and BiO6 octahedral units [27]. The bismuth borate system has specific properties, such as non-hygroscopic, high density, high optical basicity, large polarizability, and a high refractive index. In addition, the phonon energy of heavy metal oxide glass can enhance the chemical durability and radiation shielding performance [28].

On the other hand, nanocrystal-containing glasses have attracted research attention in recent years because nanocrystals have a large surface area and, therefore, they are much more reactive than their bulk counterparts [29]. The doping of nanocrystals inside glass can greatly improve the mechanical performance of glasses [30], which is good for future device fabrication. In this study, Ta2O5 nanocrystals were synthesized using the hydrothermal method, and their influence on glass structure, specifically, their mechanical, magnetic, and radiation shielding of Ta2O5-doped heavy metal oxide diamagnetic glasses, was investigated.

2. Experiments

2.1. Synthesis of Ta2O5 Nanocrystal

In a typical synthesis procedure, 0.4888 g of tantalum pentachloride TaCl5 (99.8% Sigma Aldrich) was added to 45 mL of anhydrous benzyl alcohol. The solution was firstly subjected to ultrasound for 20 min and then magnetically stirred for 30 min to get a completely dissolved mixture. The mixture was then transferred to a 100 mL Teflon-lined
stainless steel autoclave and carefully sealed. The solvothermal reaction in the autoclave was heated to 220 °C by 2 °C/min and kept for 72 h. After cooling to room temperature, the resulted cloudy suspensions were centrifuged at 4500 rpm for 15 min to retrieve the product. Repeated washing with acetone and ethyl alcohol was performed to remove possible organic impurities. The product was subsequently dried in air at 70 °C for 4 h. The off-white final product was thermally treated at 600, 800, and 1000 °C by 10 °C/min and residual for 5 h.

2.2. Fabrication of Ta$_2$O$_5$-Doped Glasses

Transparent glasses were fabricated by using reagent grade PbO, Bi$_2$O$_3$, H$_3$BO$_3$, and as-synthesized Ta$_2$O$_5$, which was prepared at 600 °C with a size of around 30 nm. The stoichiometric compositions of the batch materials (20 g) were 40PbO–45Bi$_2$O$_3$–(15–x) H$_3$BO$_3$–xTa$_2$O$_5$, where x = 1, 5, and 10 mol.%; the corresponding glasses were labeled as PBT$_0$ (host), PBT$_1$, PBT$_5$, and PBT$_{10}$. The batch was well mixed in a mortar and the mixture was melted in a gold (95% Pt–5% Au) crucible at 1000 °C for one hour. The glasses were obtained by quenching the melt on a brass mold, and then subjected to annealing at 50 °C higher than the glass transition temperature for 4 h to release the thermal stress that was produced during the quenching process.

2.3. Characterization of Samples

The crystallinity and phase of samples were characterized by X-ray diffraction (Bruker, D8 Discover system) with a Cu-Kα 1.54056 Å wavelength X-ray source. The morphologies and sizes of the nanocrystals were examined by scanning electron microscopy (TEM, FEI, Quantinspect 200). Raman and Fourier-transform infrared spectroscopy (FT-IR) spectra were recorded using an MKI Renishaw Raman spectroscopy and Varian Cary500, respectively, with a resolution range of ±0.5 cm$^{-1}$ and a KBr medium prepared with 0.5 wt% of the sample. The Vickers hardness of the glasses was tested using a 136° pyramidal diamond indenter applied to the glass at a weight load of 150 g. According to the square indent formed on the glass surface, Vickers hardness can be calculated through the following formula: $HV = 0.1891 F / d^2$, where $F$ is the applied load and $d$ is the diagonal of the indentation. The chemical valence energy was recorded using X-ray photoelectron scanning (XPS, ESCALAB 250) spectroscopy with a monochromatic Al K X-ray source ($hv = 1486.6$ eV). The obtained binding energies (BEs) were calibrated with that of an adventitious carbon (C1s) core level peak at 284.6 eV as a reference. The magnetic property of the glasses was evaluated by a vibrating sample magnetometer (VSM) instrument.

A radiation shielding characteristics test was carried out to assess the gamma ray shielding capacity of the glasses [28]. A 10 cm collimator of lead and silt with a 2 cm diameter was used to collimate the incident gamma photons emitted from a mono-energetic gamma ray source of $10^6$ photons per minute. Figure 1 shows the schematic diagram of the radiation shielding measurement. The distance between the detector and the source was 15 cm. The mass attenuation coefficient (MAC) of lead used in this instrument is $1.306 \times 10^2$ (0.015 MeV), $7.102 \times 10^{-2}$ (1 MeV), and $4.972 \times 10^{-2}$ (10 MeV). The half-value layer (HVL) of lead is 4.8 mm and the $Z_{eff}$ of lead is 82.

The Monte Carlo (MCNP-5) simulation code was applied to assess the gamma ray shielding capacity for the fabricated glasses [14]. The MCNP simulation geometry and the input file are shown in Figure 1. The applied geometry was shielded from the outer environment by a cylinder of lead with a 5 cm thickness. Then, a collimator of lead with a length of 10 cm and a silt diameter of 2 cm was used to collimate the incident gamma photons emitted from a mono-energetic gamma ray source. The mono-energetic source was set up to emit $10^6$ photons per min in the +Z direction. The made glasses were placed between the gamma ray supply and the detector. In the present simulation process, glass in this study acted as a shielding material, while bulk Pb blocks avoided the scattered photons. The F4 tally mesh detector was used to count the high-energy photons intensities and estimate the average track length. The glass was located between the radiation source...
and the detector, and the distance between the source and the detector was 15 cm. The simulation was carried out, and the recorded data has a relative error of less than 1%, as shown in the output sheets of the MCNP code [15].

Figure 1. Schematic diagram with simulation geometry of the radiation shielding measurement.

3. Results and Discussion
3.1. Structure of Ta$_2$O$_5$ Nanocrystals

The physical properties of nanocrystal-doped glasses depend on the size, shape, and properties of the nanocrystals. Therefore, we firstly investigated the structure of synthesized nanocrystal. Figure 2a–c show the XRD pattern of samples prepared at 600 °C, 800 °C, and 1000 °C, respectively. Both the 600 °C and 800 °C obtained samples show intense diffraction peaks at 2θ = 22.75°, 24.88°, 36.79°, 46.78°, 50.35°, 55.70°, 58.90°, and 64.03°; these peaks correspond well to the planes of (001), (100), (101), (002), (110), (102), (200), and (201) of the hexagonal phase of β-Ta$_2$O$_5$, respectively (JCPDS # 0019-1299) [31]. The lattice parameters $a = b = 3.6239$, $c = 3.8803$, $\alpha = \beta = 90^\circ$, and $\gamma = 120^\circ$ belong to the spatial group P6/mmm [28]. This XRD pattern indicates that Ta$_2$O$_5$ prepared at 600 °C and 800 °C is well-crystallized as hexagonal β-Ta$_2$O$_5$ phase [30]. The sample produced at 1000 °C shows diffraction peaks at 2θ = 22.84°, 28.40°, 36.74°, 44.75°, 46.75°, 49.75°, 50.70°, 55.68°, 58.44°, and 63.87°, relating to the (001), (1110), (1111), (340), (002), (0220), (2151), (1112), (2220), and (2221) planes of an orthorhombic phase of β-Ta$_2$O$_5$, respectively (JCPDS # 25-0922).

The lattice parameters $a = 6.1982\text{Å}$, $b = 3.6629\text{Å}$, $c = 3.8900$, and $\alpha = \beta = \gamma = 90^\circ$ belong to the spatial group A/mmm [8]. The phase change from hexagonal into orthorhombic is evidenced by the diffraction peak splitting at 2θ = 28.38° (100) into 2θ = 28.22° (1100) and 28.40° (1110). Another splitting of the peak occurs at 2θ = 50.35° (110), which is split into 50.70° (2151) and 49.75° (0220). The (340) plane of orthorhombic β-Ta$_2$O$_5$ at 2θ = 44.75° is very weak in this study.

The average size of the nanocrystals was calculated using the Debye–Scherrer Equation (1):

$$D = \frac{K\lambda}{\beta\cos\theta}$$  \hspace{1cm} (1)

where $K$ is a dimensionless shape factor of 0.9, $\lambda$ is the X-ray wavelength, $\beta$ is the line broadening at half the maximum intensity, and $\theta$ is the Bragg angle. After calculation, the sizes of the nanocrystals obtained at 600 °C, 800 °C, and 1000 °C temperatures were 20.8, 21.06, and 22.12 nm, respectively. The higher temperatures accelerated the aggregation of nanocrystals and induced an increase in size. On the other hand, the highly polarized Ta$^{5+}$ ions also contributed to the increase in the nanocrystal size.
Raman spectroscopy is commonly used in chemistry to provide a structural fingerprint by which molecules can be identified. In order to give an in-depth study on the structure of Ta$_2$O$_5$ nanocrystals, Raman spectra were recorded, which provided characteristic vibration modes of Ta$_2$O$_5$ nanocrystals. Figure 2d–f show the Raman spectra of Ta$_2$O$_5$ prepared at 600 °C, 800 °C, and 1000 °C, respectively, which show the structural phase transition from low-symmetry hexagonal to orthorhombic Ta$_2$O$_5$. Generally, the low-energy < 100 cm$^{-1}$ phonon modes originate from interactions between different Ta polyhedral and Ta$_6$O$_{12}^{6+}$ clusters [31]. The mid-energy Raman bands (100–400 cm$^{-1}$) correspond to O–Ta–O bending vibrations in octahedral TaO$_5$. The higher energy bands (400–800 cm$^{-1}$) could be associated with the coupled modes mainly involving the stretching of various Ta–O bonds. The higher wavenumber > 800 cm$^{-1}$ is related to the stretching vibration of Ta–O–Ta bonds [32]. It can be seen from Figure 2f that the lowest wavenumber vibration Bands 1 to 3 are sharp and intense in Ta$_2$O$_5$ prepared at 1000 °C, while these bands disappear for Ta$_2$O$_5$.
prepared at 600 °C and 800 °C. These results indicate that the Ta polyhedral and Ta_{6}O_{12}^{6+} clusters existed in Ta_{2}O_{5} prepared at 1000 °C due to the higher temperature. The vibration information are provided in Table 1.

Table 1. Raman peak parameters from the deconvolution of the Raman spectrum of the samples.

| Bands | Wavenumber (cm\(^{-1}\)) | Vibration Modes |
|-------|---------------------------|-----------------|
|       | 600 °C | 800 °C | 1000 °C |                           |
| 1     | /      | /      | 51     | External ionic vibration motion, Ta_{6}O_{12}^{6+} cluster |
| 2     | /      | /      | 78     |                           |
| 3     | /      | /      | 94     |                           |
| 4     | 124    | 124    | 124    |                           |
| 5     | /      | 196    | 245    | Bending (deformation) vibration of Ta–O–Ta bonds |
| 6     | 269    | 269    | 269    |                           |
| 7     | /      | /      | 338    |                           |
| 8     | 499    | 494    | 408    |                           |
| 9     | /      | /      | 562    |                           |
| 10    | 642    | 642    | 642    | Stretching vibration of Ta–O bonds |
| 11    | /      | /      | 711    |                           |
| 12    | /      | /      | 780    |                           |
| 13    | 883    | 883    | 883    | Stretching vibration of Ta–O–Ta bonds |

Therefore, from the comparison of the XRD and Raman spectra of three samples, the Ta_{2}O_{5} prepared at 800 °C exhibits promising size, morphology, and structure, and this sample was used as a dopant for the glasses.

3.2. Morphology and Structure of Ta_{2}O_{5}-Doped Glasses

The morphology and nanocrystal distribution inside glass are important for glass properties. Therefore, TEM images of glasses were taken to provide the morphology and distribution of the nanocrystals. As mentioned in the experimental part, the Ta_{2}O_{5} prepared at 600 °C with a size of about 20 nm was selected as the dopant to glasses, only varying with the dopant amounts of 1%, 5%, and 10%. After doping into the glass, different amounts of Ta_{2}O_{5} experienced the 1000 °C melting, combined with the deformation of space and pressure resulting from the quick temperature gradient. Therefore, doped nanocrystals (same size before doping) presented differences in size, shape, solubility, and even crystal phase. Transparent and yellowish glasses containing Ta_{2}O_{5} nanocrystals were obtained and the photographs and SEM morphology images are shown in Figure 3a–c. All glasses contain nanocrystals with sizes ranging from 20 nm (PBT\(_{1}\)) to 24 nm (PBT\(_{5}\) and PBT\(_{10}\)). The presence of nanocrystals and the varying crystal sizes result in the transparency slightly decreasing as the doping amount increases. The insets of Figure 3a–c shows the nanocrystal distribution inside the glass matrix, which confirms the particle sizes from the SEM observations, revealing that the nanocrystal size is not doping concentration-dependent.

The structure of glass after the doping of the Ta_{2}O_{5} nanocrystals inside the glasses was influential to the properties. The structures of the glasses were studied using XRD, FT-IR, and Raman spectra, which are shown in Figure 4a–d, respectively. It can be seen that glass PBT\(_{1}\) shows a halo and a broad main peak in Figure 4a at 28.84°, illustrating the amorphous glassy nature. However, small and weak signals of peaks appear at 2\(\theta\) = 22.84°, 28.40°, 36.74°, 46.75°, 50.70°, 55.68°, and 58.44°. According to the study on JCPDS #25-0922, they are related to the (001), (1110), (1111), (002), (0220), (0221), and (2220) planes of an orthorhombic phase of \(\beta\)-Ta_{2}O_{5}, respectively [33]. These peaks also appear in PBT\(_{5}\) with a slightly increasing intensity. These observations suggest that even though undissolved Ta_{2}O_{5} crystals existed, the whole matrix of PBT\(_{5}\) still has a glassy character. Different from PBT\(_{1}\) and PBT\(_{5}\), PBT\(_{10}\) exhibits sharp and intense XRD peaks, suggesting an obvious crystalline tendency in the matrix, which was probably caused by the highest undissolved Ta_{2}O_{5} nanocrystals in the matrix.
Figure 3. TME images of PBT$_1$ (a), PBT$_5$ (b), and PBT$_{10}$ (c) and their photographs, the insets are nanocrystal distribution inside glasses.

Figure 4b shows the FT-IR spectra of three samples, which show 7 absorption peaks (and 2 more in the inset). The absorption peak at 422 cm$^{-1}$ was due to the bending vibration of the tetrahedral PbO$_4$ groups, and peaks at 473 cm$^{-1}$ and 719 cm$^{-1}$ are attributed to the bending and symmetric stretching vibration of Bi–O bonds in BiO$_3$ pyramidal units, respectively [34]. The weak peak at 908 cm$^{-1}$ was caused by the stretching vibration of B–O bonds in BO$_4$ units, which is apparent in PBT$_1$ but gradually weakens as the doping amount increased [35]. The peak at 1160 cm$^{-1}$ is from the asymmetric stretching vibration of B–O bonds in BO$_3$ pyramidal units, which shifted to a lower wavenumber side as the doping amount increased, indicating the conversion of BO$_4$ to BO$_3$ [35]. Considering that all glasses were fabricated in air, water can be present in glasses. Other peaks at 2911 (very weak) and 3463 cm$^{-1}$ are related to the stretching vibration of OH bonds in the samples. A weak peak around 1630 cm$^{-1}$ is due to the bending vibration mode of OH groups [36]. The inset of Figure 6b shows the amplified wavenumber between 600–700 cm$^{-1}$; one peak at 668 cm$^{-1}$ is related to the Ta–O–Ta vibration in TaO$_6$ octahedral units, which appears in three samples, but peak at 648 cm$^{-1}$, related to the tantalum clusters, appears only in
PBT_{10}, which usually appears at a high Ta_{2}O_{5}-concentrated sample [9]. The appearance of a peak at 648 cm^{-1} also indicates that TaO_{6} aggregates in a network, which could rapidly increase the size and numbers of Ta_{2}O_{5} nanocrystals. This explains why the grain size and numbers of Ta_{2}O_{5} in PBT_{10} are obviously larger than others in the TEM observation (Figure 3).

![Figure 4](image_url)

**Figure 4.** XRD pattern (a), FT-IR spectra (b), Raman (c), and Raman deconvolution (of PBT_{10}) (d) of three samples.

Figure 4c shows the Raman spectra of three samples between wavenumbers of 0 and 700 cm^{-1}. 7 Raman bands with different intensities at 73, 99, 124, 250, 314, 537, and 660 cm^{-1} were observed in amplified Raman spectra (Figure 4d). The band at 73 cm^{-1} and 99 cm^{-1} belong to the boson peaks of glass, while the band at 124 cm^{-1} is attributed to the heavy metal Pb–O symmetric stretching vibration in PbO_{4} tetrahedral groups [37]. The band at 314 cm^{-1} is due to the Bi–O–Pb, Pb–O–Pb, Pb–O–Bi stretching linkages. The band centered at 537 cm^{-1} is attributed to the stretching vibration of Bi–O in BiO_{3} pyramidal units. The Raman frequency around 250 cm^{-1} is assigned to O–Ta–O bending vibration in TaO_{6} octahedral units, while the band at 660 cm^{-1} is from the stretching of Ta–O–Ta linkage vibrations [32], and the intensities of both bands increased with the doping amount, indicating that Ta_{2}O_{5} nanocrystals exist as TaO_{6} units in a glass network.

The appearance of Ta–O–Ta vibrations and corresponding changes to BO_{4} and BO_{3} suggest that the tantalum atoms in PBT_{1} participated in the glass network, resulting in higher network connectivity due to the high BO_{4} content. PBT_{5} remains glassy in nature even with more Ta_{2}O_{5} crystals. A large amount of Ta atoms in PBT_{10} bonded to the TaO_{6} units are responsible for forming tantalum oxide-rich regions (tantalum clusters), promoting the deformation and distortion of the network.

### 3.3. Chemical and Physical Properties

In order to verify the roles of tantalum in the structures of different samples in terms of the oxygen bonds of the network, XPS analysis was carried out and the results are shown in Figure 5. Figure 5a is the outline of the XPS core level energy of the Pb4f, Pb4d,
Bi4f, Bi4d, Ta4d, Ta4p, O1s, and B1s of the PBT_{10} sample. Among them, the O1s and B1s are most sensitive to structural changes induced by the doping of Ta_{2}O_{5}. It is well known that tetrahedral BO_{4} units play an important role in strengthening the network, while on the contrary, triangular BO_{3} units are not helpful for glass stability [38]. For the same reason, glass with good connectivity would have more bridging oxygen bonds (BO). When these BOs are broken into non-bridging oxygen bonds (NBO) by modifiers or other impurities, glasses will lose their stability and present poor chemical, mechanical, and thermal properties. In this context, the O1s and B1s were studied to get the coordination and oxygen bonds information.

Figure 5. XPS core level energy outline (a) of B1s (b) and O1s (c) of the PBT_{1}, PBT_{5}, and PBT_{10} glasses, respectively.

Figure 5b shows the B1s spectrum with the main peak located at the binding energy range of 190–194 eV. With the increase of Ta_{2}O_{5} amounts, the whole peak progressively shifts toward the lower binding energy side (gray dotted line for a guide). For example, the binding energy of B1s of PBT_{1} is located at 192.7 eV, while it shifts to 192.3 eV for PBT_{5} and...
191.9 eV in PBT10. It is well known that B\(^{3+}\) ions can form two coordination bonds (BO\(_3\) and BO\(_4\)) in a glass network, and the BO\(_4\) units have higher binding energy than that of BO\(_3\) groups [39]. Therefore, the decrease in binding energy indicates a decrease in BO\(_4\) and an increase in BO\(_3\). This conclusion is also confirmed by the deconvolution of B1s peaks. It can be seen that the area of BO\(_4\) gradually decreased with the doping amount and reached the minimum in PBT\(_{10}\); meanwhile, the BO\(_3\) increased. This result matches well with the observation of the FT-IR bands at 908 cm\(^{-1}\). Since triangular BO\(_3\) usually is less stable than tetrahedral BO\(_4\), PBT\(_1\) and PBT\(_5\) glasses are more stable than PBT\(_{10}\).

The conversion of BO\(_4\) to BO\(_3\) coordination numbers will yield free non-bridging oxygen and, accordingly, influences the oxygen bonds in glass. Figure 5c shows the core level energy of O1s with Gaussian deconvolutions. As shown in Figure 5c, there is one main peak located at the 527–535 eV binding energy of the O1s spectra in PBT\(_1\) and PBT\(_5\) glass samples. According to previous works [26], the main peak of the O1s spectrum has two contributions: bridging oxygen (BO) and NBO atoms. The NBO atoms are located at low binding energies of 529–531 eV, while BO atoms correspond to higher binding energies of 531–533 eV [26]. From Figure 4c, the O1s XPS spectra remarkably shift towards lower energies, demonstrating that excessive Ta\(_2\)O\(_5\) increases the degree of polymerization of glass structure.

As can be seen from TEM images in Figure 3, even though all samples contain nanocrystals, the structure deformation of PBT\(_{10}\) is the most remarkable, which provides low viscosity and quicker heat flow through the matrix, and speeds up the growth of residual Ta\(_2\)O\(_3\) crystals, leading to the rapid increase in size and/or numbers. These residual nanocrystals are regarded as nucleating centers in the matrix and, therefore, they decrease the ability against devitrification.

Figure 6 shows the relationship between Vickers hardness of the non-bridging oxygen and other physical parameters. Structural properties, such as the density, oxygen packing density, and optical basicity values, were calculated using the expressions reported in the literature [9] and interpreted with the physical properties of Ta\(_2\)O\(_5\)-embedded glasses. From Table 2 and Figure 6, apparently, the present samples’ density and optical basicity increased progressively with the addition of Ta\(_2\)O\(_5\) content, indicating the high compactness of the glass structure. The higher molecular weight and higher optical basicity of Ta\(_2\)O\(_5\) helped to enhance these two parameters. The oxygen packing density (OPD) firstly increased and then decreased with the increase in the doping amount, indicating that the non-bridging oxygen occurred for TPB\(_{10}\) glass. This matches well with the XPS observation. From the comparison of physical parameters, the TPB\(_5\) (green dash circle in Figure 6b) presents promising physical and mechanical performance.

![Figure 6b](image_url)

Table 2. The ratio of BO\(_4\)/BO\(_3\) and BO/NBO from the calculation of the XPS deconvolution area, Vickers hardness of samples (HV), density (\(\rho\)), oxygen packing density (OPD), and optical basicity (\(\Lambda_{\text{th}}\)).

| Samples | BO\(_4\)/BO\(_3\) | BO/NBO | \(\rho\) (gcm\(^{-3}\)) ± 0.01 | OPD ± 0.01 | HV ± 0.01 | \(\Lambda_{\text{th}}\) ± 0.001 |
|---------|-----------------|--------|--------------------------|-----------|----------|-------------------|
| PBT\(_1\) | 78/22           | 55/45  | 7.26 ± 0.00              | 98.22     | 477.55   | 1.107             |
| PBT\(_5\) | 76/24           | 53/47  | 8.11 ± 0.00              | 98.48     | 479.44   | 1.168             |
| PBT\(_{10}\) | 15/85           | 40/60  | 8.14 ± 0.00              | 90.05     | 446.88   | 1.204             |

Figure 7 shows the Vickers hardness test indentations on the glasses. It can be seen that the host glass, without any crystals, presents a complete indentation; its edges and surrounding surface are not damaged and the Vickers hardness is 467.98 HV. Similar indentation profiles can be seen for the PBT\(_1\) and PBT\(_5\) glasses with an increase of hardness, respectively. Such enhancement of the hardness for the TPB\(_1\) and TPB\(_5\) glasses is mainly due to the network former role of Ta\(_2\)O\(_5\), as confirmed by the Raman and FT-IR studies, which strengthened the crosslink of the network through its big molecule weight and network former nature. However, the PBT\(_{10}\) presents a much bigger indentation with the surrounding surface seriously damaged, and the hardness decreased to 446.88 HV as well. The deterioration of mechanical properties of PBT\(_{10}\) was caused by the large nanocrystals and tantalum clusters (refer to the Raman analysis) inside the matrix, which cracked the
nucleus and broke the homogeneity of the matrix. When a load is applied, cracks spread to its surrounding area. This also proves that the doping amount of nanocrystals higher than 5% is not good for glass mechanical stability.

![Graphs showing bridging oxygen percentage and Vickers hardness](image)

Figure 6. Composition dependence of bridging oxygen numbers, Vickers hardness (a) and density, OPD, and optical basicity (b) of glasses.

![Vickers hardness indentations on glasses](image)

Figure 7. Vickers hardness indentations on the host (a), 467.98 HV, PBT1 (b), PBT5 (c), and PBT10 (d).

3.4. Radiation Shielding Property

From the above studies on density, OPD, and hardness, it is found that Ta$_2$O$_5$ nanocrystals enhanced the compactness and mechanical performance, which are helpful for improving the radiation shielding as well. Therefore, the radiation shielding properties were studied, among which the attenuation coefficient is important. The linear attenuation coefficient values ($\mu$) indicate the probability of eliminating a photon that occurred due to the exposure of the sample to certain energy per path unit. In this study, the $\mu$ was measured experimentally at 0.015, 0.05, 0.08, 0.3, 0.5, 3, 5, and 10 MeV photon energies by using the Beer–Lambert Equation [26]:

$$\mu = \frac{\ln \left( \frac{I}{I_0} \right)}{t} \text{ cm}^{-1} \quad (2)$$
where $I$ is the intensity of the transmitted $\gamma$ ray and $t$ is the sample thickness. $\mu_m$ is related to $\mu$ and glass density $\rho$ according to Equation (3) [39]:

$$\mu_m = \frac{\mu}{\rho} = \sum f_i \left( \frac{\mu}{\rho} \right)_i \text{cm}^2/\text{g}$$  \hspace{1cm} (3)

where $f_i$ is the weight fraction and $(\frac{\mu}{\rho})_i$ is the mass attenuation coefficient $\text{MAC}$ of the $i$th element [28]. The relative deviation ($RD$) between the data and simulation can be calculated from Equation (4). The calculated data are reported in Table 3.

$$RD = \frac{(\langle \mu/\rho \rangle_{\text{MCNP}} - \langle \mu/\rho \rangle_{\text{XCOM}})}{\langle \mu/\rho \rangle_{\text{MCNP}}} \times 100\%$$  \hspace{1cm} (4)

Table 3. Mass attenuation coefficients (MAC) (cm$^2$/g) comparison of the MCNP and XCOM of the glasses.

| Energy (MeV) | PBT$_1$  | PBT$_5$  | PBT$_{10}$ |
|-------------|----------|----------|------------|
|             | MCNP     | XCOM     | RD (%)     | MCNP     | XCOM     | RD (%)     | MCNP     | XCOM     | RD (%)     |
| 0.015       | 26.854   | 27.002   | 0.022      | 28.633   | 28.712   | 0.016      | 32.003   | 32.012   | 0.014      |
| 0.05        | 4.841    | 4.874    | 0.832      | 4.944    | 4.963    | 0.842      | 5.211    | 5.241    | 0.811      |
| 0.08        | 4.638    | 4.750    | 0.797      | 5.309    | 5.505    | 0.718      | 5.442    | 5.653    | 0.38       |
| 0.3         | 0.122    | 0.132    | 0.819      | 0.123    | 0.135    | 0.975      | 0.146    | 0.156    | 0.224      |
| 0.5         | 0.088    | 0.089    | 0.011      | 0.090    | 0.091    | 0.011      | 0.090    | 0.092    | 0.022      |
| 3           | 0.050    | 0.051    | 0.291      | 0.060    | 0.062    | 0.272      | 0.061    | 0.063    | 0.413      |
| 5           | 0.027    | 0.027    | 0.228      | 0.028    | 0.028    | 0.231      | 0.028    | 0.030    | 0.230      |
| 10          | 0.026    | 0.026    | 0.191      | 0.027    | 0.027    | 0.183      | 0.028    | 0.029    | 0.172      |

Figure 8a plots the MAC versus different radiation energy points, which reached the maximum level at 0.015 MeV, varying in the range of 26.854–32.012 cm$^2$/g for PBT$_1$ to PBT$_{10}$, respectively. Gamma rays interacted with the matter by photoelectric absorption (PE), Compton scattering (CS), and pair production [18–20,23] which contributed to the $\mu_m$ value. Due to the prevalence of photoelectric interaction in the low energies, the values of $\mu_m$ suffered a rapid reduction with the increase of photon energies. This fast drop trend was caused by the PE cross-section varied with $E^{-3.5}$ [16–20,40]. At around 0.08 MeV, the MAC values for all glasses had abrupt progress due to the X-ray K-edges of Pb and Bi, and the highest absorption peak kept constant due to the fixed molar content of Pb$^{2+}$ and Bi$^{3+}$ in all the samples. At higher gamma photon energy (0.3–3 MeV), the probabilities of the CS interaction increased and predominates. Thus, the $\mu_m$ values have a moderate drop trend with an increase in the incident gamma photon energy because the CS cross-section varied with $E^{-1}$, which can be seen from Equation (5).
The Compton Scattering effect can be expressed by the following formula:

\[
\frac{1}{E'} - \frac{1}{E} = \frac{1}{E_0} (1 - \cos \theta),
\]

where \(E'\) is the energy of the scattered photon, \(E\) is the energy of the incident photon, and \(\theta\) is the scattering angle. The \(E\) and \(E'\) as a function of \(\theta\) can be easily measured with a photomultiplier detector and multichannel analyzer system. A plot of measurements of \(\frac{1}{E} - \frac{1}{E_0}\) versus measurements \((1 - \cos \theta)\) should result in an almost linear graph slope as the inverse of the electron’s rest energy \(\frac{1}{E_0}\).

Figure 8b shows the energy-dependent cross-section of the glasses. It is known that the interaction cross-sections for the pair production vary with \(\log I\) [41]. The minimum \(\mu_m\) value appears at higher gamma photon energies of 10 MeV, varying between 0.026 and 0.015 \(\mu m\) at 0.015 MeV gamma photon energy with 0.008 and 0.010 cm MFP for all glasses. Therefore, the radiation shielding effect of \(Ta_2O_5\) doping is much more remarkable at low photon energies, and the CS process domination mitigated the effect at high photon energies. In addition, at each photon energy point, the \(\mu_m\) value of the sample increased with the doping amount, indicating that the \(Ta_2O_5\) doping enhanced the shielding ability.

The mean free path (MFP), defined as \(MFP = 1/\mu_i\), was evaluated regarding the gamma photons’ simulated average track length for \(Ta_2O_5\)-doped glasses. Figure 9 displays the MFP at different incident gamma photon energies. We noticed that the lowest MFP values appeared at 0.015 MeV gamma photon energy with 0.008 and 0.010 cm MFP for all glasses. After that, owing to the PE interaction in low gamma photon energy, the MFP values increased rapidly with the increase of gamma photon energy. Due to the predominance of the CS interaction over 0.3 MeV, the MFP increased moderately with the rise of the gamma photon between 0.3 to 1 MeV. When the energy reached several MeV, the MFP varied slowly with increasing of energy. Subsequently, the MFP began to decrease when the energy was above 10 MeV due to the PC interaction. The MFP’s simulated values were augmented to the higher MFP around 10 MeV and were between 4.14, 5.02, and 5.58 cm for the TPB1, TPB5, and TPB10 glasses, respectively, indicating that the doping of \(Ta_2O_5\) decreases the MFP value.
From Table 3, the simulated average track length for Ta2O5-doped glasses. Figure 9 displays the database with an inverse proportion to $E^{3.5}$ [28]. Above 0.8 MeV, where the CS was the primary interaction, $Z_{\text{eff}}$ reduced moderately with an increase in the gamma photon energy. Above several MeV, where the PC was the primary interaction, $Z_{\text{eff}}$ began to slowly increase, with a boost in gamma photon energy due to the PC cross-section, which varied with $\log E$ [24]. The maximum $Z_{\text{eff}}$ values were obtained around 0.089 MeV due to the K-edges of the lead and bismuth elements. Among the present samples, the PBT10 sample exhibits the highest $Z_{\text{eff}}$ due to the highest Ta2O5 content, indicating that Ta2O5 increases the interaction between glass and radiation energy, resulting in less energy leaking out to the environment.

The half-value layer (HVL) is the thickness of the materials that rescues the intensity of radiation to half its original value, which is defined as $HVL = \ln 2 / \mu$. A lower HVL value points out high gamma rays’ shielding capacity. Figure 10a shows the plot of the HVLs of the glasses at different energy points, which prominently decreased as the Ta2O5 doping amount increased. On the other hand, the HVL value increased obviously with the energy of gamma photons.

From above studies, it can be seen that the highest MAC, HVL, and $Z_{\text{eff}}$ of the present study are 32.012 cm$^2$/g, 0.0035–3.322 cm, and 30.5 at 0.015 eV, respectively. These data are reasonable and good if we compare them to the pure lead bulk ($MAC, HVL, and Z_{\text{eff}}$ of 130.6 cm$^2$/g, 4.8 mm, and 82) at the same at 0.015 eV energy.

Figure 9. The mean free path (MFP) of glasses at different incident gamma ray energy.
It can be seen that the magnetization of BMT in Figure 11a is superparamagnetic without any magnetic saturation and coercivity [4]. Commonly, coercivity $H_c$ is a property of magnetic materials. It is associated with the increase of magnetic anisotropy, which depends not only on intrinsic characteristics of the crystal but also on extrinsic properties, such as shape, size, and doped magnetic ions [42]. In addition, the coercivity increases with magnetic anisotropy because the applied field (at a given temperature) can alter the orientation of magnetization. The energy barrier for coercive can be given by the Equation (8).

$$E_v = K V s_i n^2 \theta$$

where $K$ is the anisotropy constant, $V$ is the volume of nanoparticles, and $\theta$ is the angle between the easy axis and the magnetization direction. It is well known that the magnetic hysteresis behavior of bulk material is strongly influenced by the multi-domain processes like domain–wall displacement and the subsequent realignment of the domain structure [43]. When the material size is reduced to the single-domain size (i.e., <25 nm, in this study), $K$ increases remarkably and leads to the increase of the energy barrier $E_v$, resulting in a sharp decrease of $H_c$ and in the almost zero $H_c$ of superparamagnetic behavior in Figure 11a.

Figure 10. $Z_{eff}$ (a), HVL (b), and RPE% (c) of three samples as functions of radiation energy. The green curves in (c) are guides.

The radiation protection efficiency (PRE) of the samples was calculated with the base $\mu$ and glass thickness ($t$), according to Equation (7):

$$PRE = \left(1 - e^{-\mu t}\right) \times 100$$

Figure 10c shows the plot of the calculated RPE% at four fixed gamma ray energies (0.015, 0.5, 5, and 10 MeV) with a thickness of 1 cm. It is clear that for low gamma ray energy (0.015 MeV) where the PE was the main interaction, values of the RPE reached the maximum and varied between 96 and 98.8% for the three samples, indicating shielding to most of the incoming photons. With an increase in the incident gamma photon energy, the RPE% gradually decreased for the fabricated glasses until 12.5–18.9% for 10 MeV radiation. From Figure 10c, the substitution of $B_2O_3$ with $Ta_2O_5$ significantly improved the RPE% of heavy metal oxide glasses (green curves in Figure 10c) due to the high density and big mass of $Ta_2O_5$. 
3.5. Magnetic Property

Usually, materials doped with a large mass dopant such as Ta$_2$O$_5$ exhibit an improved polarization character, which is helpful for magnetic and magneto-optical performance. On the other hand, glass with good magnetic and large compactness properties has generated much interest in recent years for radiation shielding and magneto-optical devices. In the case of this study, Ta$^{5+}$ has an empty $d$ shell ($d^0$ ions) and a completely occupied outermost electronic shell which are appealing to diamagnetic property of glass. In this context, the magnetic properties of Ta$_2$O$_5$ nanocrystal-doped glasses were studied. Figure 11 shows the M versus H loop at 300 K of Ta$_2$O$_5$ nanocrystal (a) and Ta$_2$O$_5$-doped glasses (b). It can be seen that the magnetization of BMT in Figure 11a is superparamagnetic without any magnetic saturation and coercivity [4]. Commonly, coercivity $H_c$ is a property of magnetic materials. It is associated with the increase of magnetic anisotropy, which depends not only on intrinsic characteristics of the crystal but also on extrinsic properties, such as shape, size, and doped magnetic ions [42]. In addition, the coercivity increases with magnetic anisotropy because the applied field (at a given temperature) can alter the orientation of magnetization. The energy barrier for coercive can be given by the Equation (8).

$$E_V = KV\sin^2 \theta$$

where $K$ is the anisotropy constant, $V$ is the volume of nanoparticles, and $\theta$ is the angle between the easy axis and the magnetization direction. It is well known that the magnetic hysteresis behavior of bulk material is strongly influenced by the multi-domain processes like domain–wall displacement and the subsequent realignment of the domain structure [43]. When the material size is reduced to the single-domain size (i.e., <25 nm, in this study), $K$ increases remarkably and leads to the increase of the energy barrier $E_V$, resulting in a sharp decrease of $H_c$ and in the almost zero $H_c$ of superparamagnetic behavior in Figure 11a.

![Figure 11. M-H loop of nanocrystals Ta$_2$O$_5$ (a) and Ta$_2$O$_5$-doped glasses (b) at room temperature.](image)

Figure 11b shows the comparison of the magnetization of the glasses. As can be noticed, the magnetization of all the samples is negatively linear to the magnetic field increasing, passing through the zero magnetic field point. This behavior indicates a typical diamagnetic character without any saturation or coercive field because of the inert gas configuration of the host ions. The magnetization increased with the doping amount. The diamagnetic nature of the glass matrix comes from the spin–orbit interaction between the $sp$–$d$ band in the diamagnetic Bi$^{3+}$ and Pb$^{2+}$ ions, whose outmost shell has paired electrons. Due to the fully occupied orbitals, such a configuration presents a strong diamagnetic...
nature. The doping of diamagnetic Ta$^{5+}$ ions increased the concentration of magnetic ions and increased the dipole moment by the spin–orbit interaction between the $d$–$d$ transition of the Ta ions and the $sp$–$d$ interaction between the Bi$^{3+}$, Pb$^{2+}$, and Ta$^{5+}$ ions. The magnetization of the atom mainly came from contributions of the orbitals, electrons, and spin angular momentum. Therefore, the doping of diamagnetic Ta$^{5+}$ ions increases the dipoles and magnetic spin movement, leading to an increase in the magnetization of the glasses.

On the other hand, the increase of magnetization is probably also due to the existence of the nanocrystals. These small nanocrystals inside the matrix acted as a highly polarized single magnetic domain, and the surface anisotropy of nanoparticles dominates the magneto-dynamics [23]. Smaller nanoparticles with a higher surface-to-volume ratio exhibit a much larger proportion of non-compensated surface spins and thus, display a higher magnetization value than those of larger nanoparticles.

Diamagnetic susceptibility is a comprehensive description of a magnetic moment for a free atom having atomic angular moment, electron spin, and diamagnetic response. Diamagnetic behavior is the change in the orbital angular momentum induced by an external magnetic field, and therefore, all materials exhibit a diamagnetic response [44]. Diamagnetic susceptibility is a property of all atoms in molecules and is proportional to the number of electrons and to the square of the radius of the orbit of a closed shell. The influence of magnetic Ta$^{5+}$ ions on diamagnetism can be studied by calculating the diamagnetic susceptibility $x_D$ according to the Pascal method, using values for the diamagnetic susceptibility of every atom ($x_D$) and bond ($\lambda_i$) in the molecule:

$$x_D = \sum_i xD_i + \sum \lambda_i$$ (9)

The $x_D$ of Pb$^{2+}$ is $(-46 \times 10^{-6}$ emu/mol), of Bi$^{3+}$ is $(-25 \times 10^{-6}$ emu/mol), of B$^3$ is $(-0.2 \times 10^{-6}$ emu/mol), of O$^{2-}$ is $(-6 \times 10^{-6}$ emu/mol), and of Ta$^{5+}$ is $(-14 \times 10^{-6}$ emu/mol) [45]. The doping of Ta$_2$O$_5$ at the expense of B$^3$ in the same molar was helpful for the total diamagnetic susceptibility of the glass based on Equation (9). The theoretically calculated diamagnetic susceptibility of TPB$_{11}$, TPB$_{12}$, and TPB$_{10}$ is 2.46, 5.88, and 9.42 $\times 10^{-6}$ emu/mol, respectively, which is very close to that of the magnetization obtained from the experiment measurements (2.21, 5.44, and 9.53 $\times 10^{-6}$ emu/mol).

4. Conclusions

$5d^0$ Ta$^{5+}$ in Ta$_2$O$_5$ has a large density, a big refractive index, and a tunable band gap, which are potentially important for luminescence, nonlinearity, and radiation shielding applications. In this study, Ta$_2$O$_5$ nanocrystals were synthesized using a hydrothermal method at 600, 800, and 1000 °C. XRD and Raman spectra revealed that the Ta$_2$O$_5$ prepared at 600 and 800 °C is $\delta$-Ta$_2$O$_5$ with hexagonal phase, while 1000 °C yielded $\beta$-Ta$_2$O$_5$ with an orthorhombic structure. A high temperature speeds up the crystal growth and the formation of Ta$_6$O$_{12}^{6+}$ clusters.

Transparent Ta$_2$O$_5$ nanocrystal-doped heavy metal oxide glasses were obtained by the melt-quenching method. SEM and EDX analysis confirmed that Ta$_2$O$_5$ exists in the glass matrix (20–30 nm). XRD, FT-IR, and Raman spectra revealed that the Ta$^{5+}$ ions entered into the glass as Ta$_2$O$_6$ octahedral units, which strengthened the network connectivity at 1–5% Ta$^{5+}$ content, while at 10% content, Ta$_2$O$_6$ played a modifier role and distorted the network through producing NBOs and converting BO$_3$ to BO$_4$ units. The 1% and 5% Ta$_2$O$_5$-doped glasses exhibited excellent mechanical hardnesses of 477 HV and 479 HV, respectively. The magnetization was greatly enhanced due to the $sp$–$d$ and $d$–$d$ interactions between the Bi$^{3+}$, Pb$^{2+}$, and Ta$^{5+}$ ions. Due to the modification of Ta$_2$O$_5$, the magnetization $x_D$ and radiation shielding efficiency were greatly improved to $x_D = 9.53 \times 10^{-6}$ emu/mol, $RPE\% = 96$–98.8%, and MAC $= 32.012$ cm$^2$/g, and $MFP = 5.02$ cm, $HVL = 0.0035$–3.322 cm, and $Z_{eff} = 30.5$ due to the increase of polarizability and the Ta$_2$O$_5$-tuned structure.
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