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Original Article

Mechanical and elastic properties of vitrified radioactive wastes using ultrasonic technique

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ABSTRACT

It is important that radioactive and nuclear wastes are immobilized in a glass composition with lower melting temperatures due to their economy. In this study, the elastic and mechanical properties of sodium borate-based vitrified radioactive waste were measured using ultrasonic techniques. Many ultrasonic parameters, such as elastic moduli, Poisson's ratio, and microhardness, were calculated by measuring the ultrasonic velocities of the glasses. The ultrasonic velocity data, the density, the calculated elastic moduli, micro-hardness, softening temperature, and Debye temperature depending on the glass composition were evaluated, and the relation with the structure was clarified. It was observed that the elastic modulus and Poisson ratio increased as the Cs_2O content increased in glasses containing Cs waste. This result shows that the rigidity of the network structure of these glasses increases in contrast to the glass containing Sr.

1. Introduction

About 15% of the worldwide electrical power is generated by nuclear power plants and that fraction will likely increase [1–3]. On the other hand, the disposal of nuclear waste produced from nuclear facilities is the most important issue both technically and politically. There are various feasible solutions to treat nuclear waste depending on the type and concentration of the radioactive waste.

The vitrified nuclear waste form is one of the most promising materials for radioactive waste management applications [4–8]. Glass is the most preferred material for the immobilization of waste forms because of its good chemical durability, sufficient mechanical properties, and radiation stability. Borosilicate glasses are well characterized for high-level waste immobilization in many studies that investigated their chemical and mechanical stability of them. Other borate-based glass compositions have been used in several studies to improve their performance of them on radioactive and industrial wastes in recent years [6,7,9].

Studies on the elastic properties which are affected by the rigidity of the structure have given significant information about the structure of the glasses. Glasses have two independent elastic constants: i) longitudinal and shear elastic moduli obtained from the longitudinal and ii) shear sound velocities and density of the glass and composite materials [10–12]. In recent years, there have been interesting studies on elastic moduli of glasses measuring the ultrasonic velocities to investigate the structure of the glasses influenced by many physical parameters [9–11]. Different parameters such as elastic moduli, Young's modulus, Poisson's ratio, Vickers hardness, and micro-hardness of the glasses can be obtained to estimate of mechanical strength of the glasses [13–18].

The main goal of this study is to focus on alternative glass compositions for the vitrification process of nuclear wastes and to present the elastic and mechanical properties of these new glass compositions using ultrasonic techniques. All glass compositions were prepared using a conventional melt-quenching method. Elastic properties have been investigated using sound velocity measurements at 4 MHz at room temperature. Some elastic properties such as Debye temperature (θ_D), the elastic moduli, Poisson's ratio, microhardness, softening temperature (T_s), and Pugh ratio, were calculated for host glass and each vitrified radioactive waste form from the longitudinal (ν_L) and shear (ν_T) ultrasonic velocities. Then, the relation between the structure of host glass and vitrified radioactive waste was clarified.

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2. Material and method

2.1. Host glass preparation and property measurements

All glass compositions were prepared by mixing all specified weights of NaOH (99.9% Fulka), and B_2O_3 (99%, Aldrich) using a conventional melt-quenching method as mentioned in our previous studies [7,8]. Commercial powders of reagent-grade chemicals were melted into an alumina crucible in an electrically heated furnace under ordinary atmospheric conditions for 1h at 900 °C. The melt was poured into an alumina mold heated at 300 °C to reduce any tendency of volatilization of the mixture. The alumina mold was kept in another furnace for annealing at 350 °C for 1 h and left to cool to room temperature while inside the furnace. The resulting glass samples were in cylindrical form, 20–25 mm in height, and 8 mm in diameter. The detailed preparation procedures for the glasses are described elsewhere [7,8]. All glass samples were carefully polished by using abrasive papers. The edges of the bars were bevelled by using fine abrasive papers. The surface areas of glass samples were calculated after measuring their length, width, and thickness with a calliper for ultrasonic measurements [7,8].

2.2. Vitrified radioactive waste forms preparation and property measurements

Experiments have been carried out with inactive strontium (Aldrich) and cesium (Aldrich) (which would simulate ^{90}Sr and ^{137}Cs) to understand the formation and volatilization of the glass [7]. The waste oxides were mixed with glass-forming additives such as NaOH, and B_2O_3. Well-mixed powders of glass formers with $30Na_2O.70B_2O_3$ compositions were produced by melting the batches in dense alumina crucibles at 950 °C for 1 h. The melt was quenched in the air by pouring it into a 22 × 8 mm graphite mold. The samples were transferred to an annealing furnace, held at ~350 °C for 30 min, and consequently furnace-cooled [7].

2.3. Density measurements for host and vitrified waste forms

The density of each prepared glass sample was determined by a simple Archimedes method using bi-distilled water at room temperature as stated in our previous study. The error in the density measurements was calculated as ± 0.005 g cm^{-3} [7,8].

2.4. Ultrasonic measurements

Elastic properties such as Young's modulus and Poisson's ratio at room temperature were measured with frequencies of 4 MHz. Elastic properties of the glasses at room temperature in the air were determined from measurements of longitudinal (ν_l) and shear (transverse) (ν_s) ultrasonic velocities. The equations for calculating various elastic constants using the velocities of the transverse and longitudinal waves are given in Eq. (1) and Eq. (2):

$$C_B = \sqrt{\frac{E}{\rho} x \frac{1-\mu}{(1+\mu)(1-2\mu)}} \tag{1}$$

$$C_B = C_E = \sqrt{\frac{E}{\rho} x \frac{1}{2(1+\mu)}} = \sqrt{\frac{G}{\rho}} \tag{2}$$

$$C_Y = \frac{0.87+1.12\mu}{1+\mu} x \sqrt{\frac{E}{\rho} x \frac{1}{2(1+\mu)}} \tag{3}$$

where, C_B: longitudinal wave velocity, C_E: transverse wave velocity, E: elasticity or Young's modulus, G: shear modulus, μ: Poisson's ratio, ρ: density [18].

Mechanical and elastic properties such as longitudinal elastic modulus (L), shear modulus (G), bulk modulus (K) and Young's (E), Deby temperature (θ_D), softening temperature T_s and Poisson ratio (σ) of host glasses and glasses containing Cs and Sr wastes were calculated from ultrasonic measurements.

Poisson's ratio was calculated using following equation [9]:

$$\sigma = 0.5 - \left(\frac{1}{7.2} V_t\right) \tag{4}$$

The Debye temperature of host glass and vitrified waste forms was calculated using the following equation [10]:

$$\theta_D = \left[\frac{3V_m^3 h^3 \varphi N_A}{4\pi K_B^3 V_M}\right]^{\frac{1}{3}} \tag{5}$$

where ν_m is the average ultrasonic velocity calculated by the following equation, h is the Planck constant, φ is the number of atoms in the chemical formula, N_A is the Avogadro number, K_B is the Boltzmann constant, and V_M is the molar volume.

$$V_m = \left[\frac{3V_l^3 V_s^3}{V_l^3 + V_s^3}\right]^{\frac{1}{3}} \tag{6}$$

It was stated by Marzouk (2009) [11] that the softening temperature (T_s) of host glass and vitrified waste forms is correlated with the ultrasonic velocity of the shear waves [10,11].

$$T_s = \frac{\nu_s M}{C^2 \varphi} \tag{7}$$

where M is the effective molecular weight and C is the proportionality constant.

Acoustic impedance Z_i is related to the transmission and reflection of sound energy in glass samples and is given in the equation below [11]:

$$Z_i = V_m \rho \tag{8}$$

The latent heat of melting ΔH_m of the host glass and vitrified waste forms is explained by the following equation [11]:

$$\Delta H = \frac{9M\theta_D^2 r_i^2 K_B^2}{128h^2} \tag{9}$$

The diffusion constant (D_i) is defined in the following equation [11]:

$$D_i = \frac{K_B \theta_D r_i^2}{96h} \tag{10}$$

where r_i is the bond length of the oxide components in the chemical composition of the host glass and vitrified waste forms.

3. Results and discussion

The immobilization of cesium and strontium wastes in a glass structure and the structural characterization and chemical resistance of glass containing waste were investigated in our previous study [7]. The immobilization of cesium and strontium wastes in a glass structure was simulated using stable salts of cesium and strontium, aiming to have a long half-life and to prevent their accidental spread in the waste area during long-term storage. In the previous study, the changes in the glass structure were evaluated by XRD, EDX, and FTIR analyses without making an evaluation such as heat production and radiation intensity of the glass [7].

In this study, the changes in the mechanical properties of the glass structure with the addition of Cs and Sr wastes into the glass structure were investigated. It has been determined that the evaluations given in detail below are in harmony with the results obtained for the chemical resistance tests of host glass and vitrified wastes in our previous study.

The density of each glass sample is an important property that indicates changes in the structure of that glass. It was stated by Doweidar and Saddeek (2009) [19] that the density is affected by changes in the geometric configuration of the glass, the coordination number, the crosslink density, and the space dimensions of the glass [19]. The densities of sodium-borate-based host and vitrified waste forms were found in the range of 3.00–3.15 g cm^3 for vitrified Sr waste glasses and 1.82–4.82 g cm^3 for vitrified Cs waste glasses while the density of host glass was 2.38 g cm^3. The increase in the density of vitrified waste glass is an indication that the BO_4 groups in the host glass have increased bonding with Cs_2O or SrO [7]. Density has been reported in the range of 3.988–4.182 g cm^{-3} for TeO_2–V_2O_5–TiO_2 glasses, 2.490–2.960 g cm^{-3} for copper-doped sodium phosphate glasses, 5.442–6.516 g cm^{-3} for xPbO.(10-x)Er_2O_3–90Bi_2O_3 glasses, 5.289–5.634 g cm^3 for Nb_2O_5–TeO_2 glasses, 5.006–5.485 g cm^3 Nb_2O_5–Li_2O–TeO_2 glasses, and 4.8670–5.2471 g cm^3 for 70TeO_2-(30-x)ZnO-xNa_2O glasses [10,11, 20–22].

The elastic modulus of the prepared glass containing host and waste was determined by measuring the speed of sound waves in the materials. The increase in the elastic modulus values is an indicator of the rigidity of the materials. The elastic modulus of the glasses containing 35SrO.65 (30Na_2O.70B_2O_3) and 20Cs_2O.80(30Na_2O.70B_2O_3) waste were found to be higher than the host glass. This result shows that the addition of Cs, and Sr wastes into sodium borate glass increases the strength of the glass.

The ratio of the Shear modulus to the bulk modulus (G/K) is called the Pugh ratio and is considered the criterion of whether the material is ductile or brittle. The critical value for this ratio is 0.57. Above the critical value, the material shows brittle properties and below this value, the material may ductile [13]. Since the G/K ratio of vitrified forms containing Cs and Sr waste is below 0.57, it can be said that they are ductile.

The Poisson's ratio (μ) is used to estimate the ductile and brittle properties of the material. Depending on the change in the waste ratio in the glasses, the variation of the Poisson ratio shows the dimensional changes in the network of the glasses [9]. It was suggested by Bogue and Sladek that fractal bond connection value (d) gives information about the effective dimensionality of the glass. This value is defined as d = 4S/K. In this equation, S, K and L are given as below [9].

$$S=\rho V_l^2 \tag{11}$$

$$L=\rho V_s^2 \tag{12}$$

$$K=L-\frac{4}{3}S \tag{13}$$

The value of d indicates that 3D networks of tetrahedral coordination polyhedral are formed when it is 3, 2D layer structures formed when it is 2, and 1D chains are formed when it is 1 [9]. In this study, the d values of the glasses containing Sr and Cs wastes are between 1.11-1.46 and 1.06–1.40, respectively. This indicates that 1B chains are formed in these vitrified waste forms. In host glass, the d value was found to be 1.94 and can be interpreted as 2D layer structures are formed. In our previous study [7], four different frequency regions were observed in the FTIR analysis of sodium borate-based glasses. Two regions in the wavelength range of 1150–1550 cm^{-1} and 800-1150 cm^{-1} give the tensile vibrations of triangular BO_3 and tetrahedral BO_4 borate structures, respectively. According to the results we obtained in our previous study, the formation of these peaks was observed in all boron-based glass samples. The band around 1200 cm^{-1} shows the tension vibrations of the B–O bands of the $(BO_3)^{3-}$ structure resulting from the linkages of the chain oxygen of different groups. It can be said that Sr and Cs wastes are bonded to the glass structure through chain oxygen in Sr and Cs-added glasses.

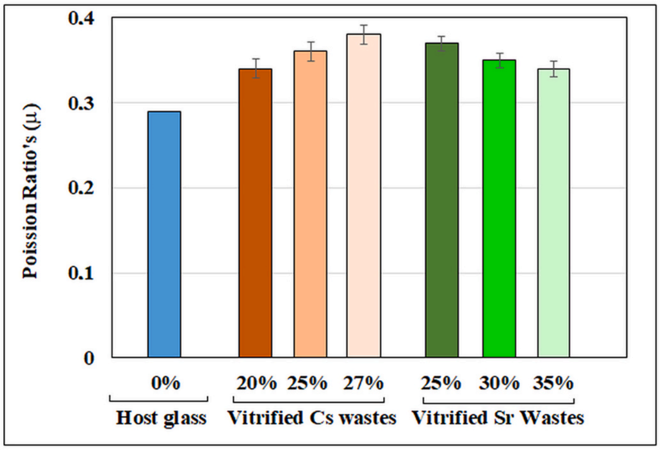

Fig. 1. Relationship between Poisson ratio and content of wastes in the glass.

Kumar et al. (2022) reported that if the Poisson's ratio is greater than 0.26, the material will be ductile, and if it is small, it will show brittle properties [13]. The Poisson's ratio of vitrified waste forms greater than 0.26 indicates that they are ductile. This supports the results found for the Pugh ratio. As seen in Fig. 1, the Poisson ratio was decreased as the Sr ratio increased in vitrified strontium form. In these glasses, this ratio varies between 0.34 and 0.37. In cesium vitrified glass, the Poisson's ratio varies between 0.34 and 0.38. Poison ratio varies for different glass compositions. Poison ratios depending on the additives added to the main structure of the glass were found in the range of 0.2176–0.2189 for TeO_2–V_2O_5–TiO_2 glasses, 0.241 to 0.261 for copper-doped sodium phosphate glasses, 0.261 to 0.285 for 70(TeO_2)–(30-x)ZnO)-x(Na_2O) glasses, 0.399 to 0.440 for xNb_2O_5–(1-x)TeO_2 glasses, 0.420 to 0.438 for 0.5xNb_2O_5–0.5xLi_2O–(1-x)TeO_2 composition glasses and 0.240 to 0.301 for xPbO-(10-x)Er_2O_3–90Bi_2O_3 glasses [10,11,20–22].

Debye temperature is an important material property resulting from the atomic vibrations of the material. The Debye temperature of each of the vitrified waste products was calculated from the measured ultrasonic velocities using equation (5). The increase in Debye temperature indicates the increase in the hardness of the host and vitrified waste form. It can be seen from Fig. 2 that there is no significant change in Debye temperature with the increase in the amount of Sr in vitrified Sr forms. In vitrified Cs forms, with the addition of 25% Cs, the Debye temperature slightly decreases compared to the host glasses, while a decrease is observed as the Cs ratio increases. Also, the variation of both latent heat of fusion and diffusion constant supports the Debye temperature gradient curve as shown in Fig. 2.

The diffusion constant (D_i) shows the temperature at which all vibration modes are excited in the glasses studied. The increase in D_i with the addition of Sr and Cs wastes to the host glass is an indication of an increase in the hardness of the waste-containing glass system. The D_i value for the glass containing Sr waste varies in the range of 6.68x10^{-9} to 6.85x10^{-9} m^2 s^{-1}. In glass containing Cs waste, this value is between 7.30x10^{-9} and 10.51x10^{-9} m^2 s^{-1}. Besides, while the latent heat of melting ΔH_m calculated from Equation (9) is 5581 J for host glasses, it ranges from 30554 J to 31533 J for the glasses containing Sr, and between 39297 J and 73767 J for the glasses containing Cs.

Hardness, one of the mechanical properties of materials, is defined as a measure of the material's resistance to permanent indentation or penetration. Microhardness (H) is calculated using Equation (14) [9].

$$H=\frac{(1-2\sigma)E}{6(1+\sigma)} \tag{14}$$

As expected, the calculated microhardness values for both vitrified waste forms were increased or decreased with a similar trend to the elastic modulus (Fig. 3). It was determined that the microhardness decreased as the waste content increased in glasses containing Cs waste. In the glass containing Sr waste, on the other hand, as the amount of waste increases, the microhardness value increases. The highest microhardness was found in vitrified waste forms containing 35% Sr waste.

Fig. 4 shows the variation of elastic modulus of glasses with different

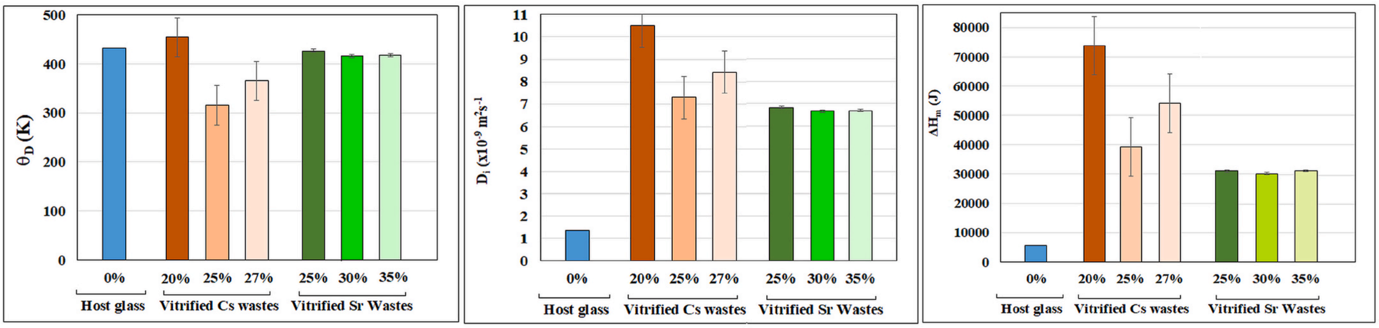

Fig. 2. Variation of Debye temperature with increasing waste contents.

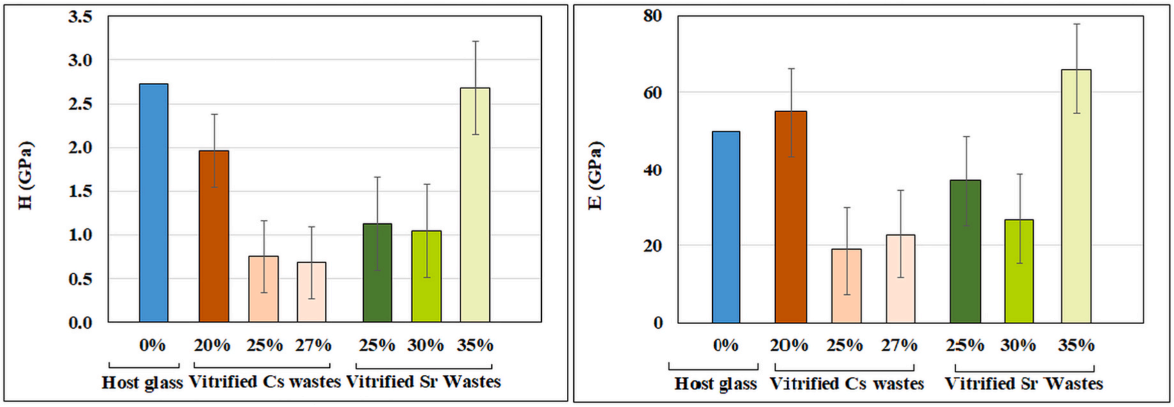

Fig. 3. Variation of microhardness with increasing waste contents and relation with elastic modulus.

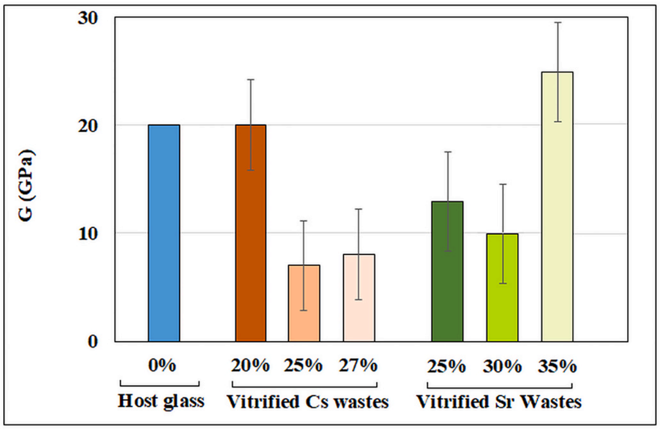

Fig. 4. Variation of elastic modulus of vitrified waste forms.

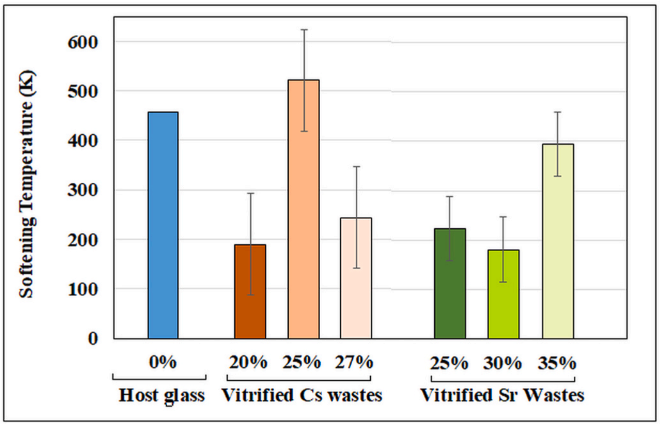

Fig. 5. Relationship of softening temperature of vitrified waste with waste content.

SrO and Cs_2O contents, such as shear modulus (G), bulk modulus (K), and Young's modulus (E). In vitrified wastes containing strontium, shear modulus, and bulk modulus increase with the increase in Sr content of glasses, while Young's modulus decreases. On the other hand, in vitrified waste containing cesium, all elastic modulus decreases with increasing Cs content.

The softening point is the temperature at which a material begins to soften. In vitrified wastes containing SrO and Cs_2O, the softening temperature increases as the waste content increases. It was determined that the softening temperature of the vitrified wastes was lower than that of the host glasses (Fig. 5).

4. Conclusions

The usability of sodium borate-based glasses in the vitrification of Sr and Cs wastes was investigated by ultrasonic technique of their mechanical strength.

The mechanical properties of sodium borate-based vitrified waste forms were evaluated in this study. It was found that the densities of glasses containing vitrified Sr waste increased with increasing %Sr content. Accordingly, the elastic modules of these glasses also increase with the increase of %Sr content. Elastic modulus values of vitrified waste forms containing 35% Sr were found to be higher than host glasses. Similarly, the chemical resistance of these glasses has been found to be the best at 35% Sr in our previous study.

On the other hand, in glasses containing Cs waste, both their densities and elastic modules decrease with the increase of %Cs content from 20% to 27%. The density and elastic modules of the glasses were found to be higher in the vitrified waste forms at a rate of 20%Cs compared to the host glasses. This result is also in agreement with the chemical resistance results reported for these glasses in the previous study.

The microhardness values of these vitrified waste forms also prove their mechanical strength at the determined waste ratios.

The fractal bond connection value (d), which gives information about the effective dimensionality of the glass, shows that the 2D layer structure in the host glasses is switched to the 1D chain structure with the contribution of Sr and Cs.

In contrast to the glass containing Sr, it is observed that the elastic modulus and Poisson ratio increase with increasing Cs_2O content in the glasses containing Cs, indicating the increase in rigidity of the network structure.

The results obtained are in good agreement with the chemical durability results obtained in our previous study of these waste-containing glasses.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

References

[1] R.K. Brow, M.L. Schmitt, A survey of energy and environmental applications of glass, J. Eur. Ceram. Soc. 29 (2009) 1193–1201, https://doi.org/10.1016/j.jeurceramsoc.2008.08.011.

[2] S. Shirvani, M.H. Mallah, M.A. Moosavian, J. Safdari, Studies of removal of uranium from wastewater by novel magmolecular process with the aim to learn for nuclear waste management, J. Radioanal. Nucl. Chem. 310 (1) (2016) 45–52, https://doi.org/10.1007/s10967-016-4789-2.

[3] J.K. Sutherland, Radioactive wastes, origins, classification and management in nuclear energy materials and reactors, in: Y.A. Hassan, R.A. Chaplin (Eds.), Encyclopaedia of Life Support Systems, United Nations Educational, Scientific and Cultural Organization, Paris, 2010, pp. 173–214.

[4] Y. Saddeek, Structural and acoustical studies of lead sodium borate glasses, J. Alloys Compd. 467 (1) (2009) 14–21, https://doi.org/10.1016/j.jallcom.2007.11.126.

[5] I.L. Pegg, Behavior of technetium in nuclear waste vitrification processes, J. Radioanal. Nucl. Chem. 305 (1) (2015) 287–292, https://doi.org/10.1007/s10967-014-3900-9.

[6] Y. Cheng, H. Xiao, W. Guo, W. Guo, Structure and crystallization kinetics of PbO-B_2O_3 glasses, Ceram. Int. 33 (2007) 1341–1347, https://doi.org/10.1016/j.ceramint.2006.04.025.

[7] S. Akyil Erenturk, M. Bengisu, C. Erdogan, Evaluation of sodium borate glasses for radioactive waste immobilization applications, J. Radioanal. Nucl. Chem. 314 (2017) 2069–2086, https://doi.org/10.1007/s10967-017-5536-z.

[8] C. Erdogan, M. Bengisu, S. Akyil Erenturk, Chemical durability and structural analysis of PbO–B_2O_3 glasses and testing for simulated radioactive wastes, J. Nucl. Mater. 445 (2014) 154–164, https://doi.org/10.1016/j.jnucmat.2013.10.025.

[9] A. Abd El-Moneim, I.M. Youssof, L. Abd El-Latif, Structural role of RO and Al_2O_3 in borate glasses using an ultrasonic technique, Acta Mater. 54 (2006) 3811–3819, https://doi.org/10.1016/j.actamat.2006.04.012.

[10] R. El-Mallawany, N. El-Khoshkhany, H. Afifi, Ultrasonic studies of $(TeO_2)_{50}$-$(V_2O_5)_{50}$-x$(TiO_2)_x$ glasses, Mater. Chem. Phys. 95 (2006) 321–327, https://doi.org/10.1016/j.matchemphys.2005.06.025.

[11] S.Y. Marzouk, Ultrasonic and infrared measurements of copper-doped sodium phosphate glasses, Mater. Chem. Phys. 114 (2009) 188–193, https://doi.org/10.1016/j.matchemphys.2008.09.021.

[12] S. Gholizadeh, A review of non-destructive testing methods of composite materials, Procedia Struct. Integr. 1 (2016), https://doi.org/10.1016/j.prostr.2016.02.008, 050–057.

[13] U. Kumar, S. Kaity, A. Arya, A. Banerjee, Characterization and thermal expansion of Th–10Zr alloy, J. Radioanal. Nucl. Chem. 331 (2022) 1619–1627, https://doi.org/10.1007/s10967-022-08217-0.

[14] L.P. Martin, E.A. Lindgren, M. Rosen, H. Sidhu, Ultrasonic determination of elastic moduli in cement during hydrostatic loading to 1 GPa, Mater. Sci. Eng. A279 (2000) 87–94, https://doi.org/10.1016/S0921-5093(99)00639-5.

[15] N. Parveen, G.V.S. Murthy, Determination of elastic modulus in nickel alloy from ultrasonic measurements, Bull. Mater. Sci. 34 (2) (2011) 323–326, https://doi.org/10.1007/s12034-011-0070-z.

[16] D. Souri, Ultrasonic velocities, elastic modulus and hardness of ternary Sb-V_2O_5-TeO_2 glasses, J. Non-Cryst. Solids 470 (2017) 112–121, https://doi.org/10.1016/j.jnoncrysol.2017.05.006.

[17] R. El-Mallawany, Quantitative analysis of elastic moduli of tellurite glasses, J. Mater. Res. 5 (1990) 2218–2222.

[18] J. Krautkramer, H. Krautkramer, Ultrasonic Testing of Materials, Springer, Berlin, 1990.

[19] H. Doweidar, Y.B. Saddeek, FTIR and ultrasonic investigations on modified bismuth borate glasses, J. Non-Cryst. Solids 355 (2009) 348–354, https://doi.org/10.1016/j.jnoncrysol.2008.12.008.

[20] Y.S. Rammah, M.S. Gaafar, S.Y. Marzouk, H. ElRashidy, I.O. Olarinoye, R. El-Mallawany, Ultrasonic waves, mechanical properties and radiation shielding competence of Er^{3+} doped lead borate glasses: experimental and theoretical investigations, J. Australas. Ceram. Soc. 57 (2021) 1163–1176, https://doi.org/10.1007/s41779-021-00614-0.

[21] A.A. El-Moneim, R. El-Mallawany, Y.B. Saddeek, Nb_2O_5–TeO_2 and Nb_2O_5–Li_2O–TeO_2 glasses: evaluation of elastic properties, J. Non-Cryst. Solids 575 (2022), 121229, https://doi.org/10.1016/j.jnoncrysol.2021.121229.

[22] R. El-Mallawany, A. El Adawy, A. Gamal, Y.S. Rammah, Experimental and theoretical elastic moduli of sodium–zinc–tellurite glasses, OPTIK - Int J Light Electron Opt. 243 (2021), 167330, https://doi.org/10.1016/j.ijleo.2021.167330.