Elastic Properties of γ-radiated Borate Glasses Using Pulse Echo Technique

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Longitudinal and shear ultrasonic velocities were measured in sodium borate glass samples of different compositions before and after irradiation with γ-rays. Measurements were carried out at room temperature and 4 MHz frequency using pulse echo technique. Densities of the glass samples were measured using displacement method while toluene was used as immersion liquid. Elastic constants were calculated as well as Debye temperature, softening temperatures and microhardness for all glass samples. The results showed that, irradiation of sodium borate glass has less noticeable change on ultrasonic velocity than the effect of increasing sodium oxide content. The increase in velocity was attributed to the gradual increase in the rigidity of the glass and, hence, strengthening of the network due to the gradual change of boron atoms from the three-fold to the four-fold coordination of oxygen atoms.

Introduction:

The propagation of ultrasonic waves in solids provides important information regarding the atomic and/or molecular motion in materials. The velocity of ultrasonic waves and, hence, the elastic properties are particularly suitable parameters for characterizing glasses as a function of their composition. Some informations about both the microstructure and elastic properties through the behaviour of the network and the modifier can be obtained.

The largest group of glasses is the inorganic oxides and their mixtures. They are commonly used because of their diverse applications in the fields of electronics, nuclear and solar energy technologies and acousto-optic devices.

Glassy materials as well as some organic ones, mainly polymers, have been increasingly tested for dosimetry purposes. They also were successfully used as detectors for different kinds of radiation [1]. γ- radiation causes changes in the physical properties of materials. The changes are strongly dependant on the internal structure of absorbing substances. As a result a transfer of the orbital electrons will occur and possibly atoms within the structure of substance.

Sodium borate glasses are composed of net-work former B_2O_3 and the modifier Na_2O. According to Bisco and Warren [2], pure B_2O_3 exists in planar three-fold coordination. The addition of net work modifier ions up to about 15% produces four-fold coordinated boron atoms by cross linking the planar triangle and would be expected to tighten and strengthen the network.. However, the results of the ultrasonic velocity measurements of Gladkov and Tarasov [3] indicated that the strengthening of the network continues up to at least 35 mol % Na_2O.

Krause and Kurkjian [4] have used the ultrasonic pulse superposition method to study the velocity of sound waves in sodium borate glasses. On the other hand, Kodama [5] studied the relationship between the elasticity and the structure of sodium borate glasses. He showed the way in which the network-former and the modifier contributed to the elasticity of these glasses. Ultrasonic velocities were measured as a function of composition, from which elastic resistances of the network former and the modifier are obtained on the basis of the theory of elastic internal energy [6]. Sidkey et al. [7] determined the ultrasonic velocity in samples of sodium borate glasses containing Na_2O between 5.6 and 27.2 mole %. Boron anomaly was studied and results showed that this anomaly should appear at compositions above 28 mol % sodium oxide.

As indicated by El Mallowany et al.[8] γ-ray radiation causes changes in the physical and chemical properties of the solid materials. These changes are strongly dependant on the interaction mechanism of γ-rays with materials. The interaction mechanism of γ-rays with glass samples mainly occurs by means of electronic excitation, electronic ionization and by primarily atomic displacement of orbital electrons. They [8] also studied γ-radiation effect on the ultrasonic attenuation in tellurite glasses and concluded that both ultrasonic absorption (α) and internal fraction (Q^{-1}) increase.

Hussein et al. [1] studied the d.c electrical conductivity of the binary γ-irradiated $MoO_3 - P_2O_5$ glass to investigate the validity of using such glass samples as γ-ray dosimeters. They found that the d.c electrical conductivity decreases with increasing γ-dose. They concluded that change in d.c. conductivity is related to the energy absorbed in the glass samples due to the irradiation. They also reported that the defects produced in glass by irradiation can be represented by the general equation:

$$\text{Defect in glass} + h\,\nu \longrightarrow \text{positive hole} + e^-$$

Sanad et al. [9] studied the effect of heat treatment and irradiation on the electrical conductivity of barium borate glass containing iron. They reported that the conductivity decreases with increasing irradiation time up to 18h, and then increases .They attributed this change to the breakage of the B-O bond formed with non-bridging oxygen atoms.

Experimental:

A series of sodium borate glass samples were selected according to the following formula, x Na_2O-(100-x) B_2O_3, where x = 2.0, 5.0, 10.4, 13.2, 18.0, 20.0, 22.0 and 27.0. The starting materials of sodium carbonate and boric acid were mixed together and calculated to give a sample of 30 gm. The specified masses of the constituent materials were mixed together and fused at 400 ^oC in a silica crucible. After complete fusion, the temperature of the muffle furnace was raised to 900 ^oC and left for two hours in order to improve homogeneity. Occasional stirring of the melt using a thin silica rod was carried out before casting. The temperature of the furnace was lowered to 350 ^oC and left for 30min. The melt was then poured into a split mold made from mild steel. Annealing was made at 300 ^oC for about 3 hr and glass samples were allowed to cool to reach room temperature 25 ^oC. The obtained samples were polished with 0.3 micron alumina powder using precision polishing machine. Two opposite sides of each glass sample were polished to obtain flat and mutually parallel faces.

The densities of the glass samples were measured to four significant figures by the displacement method using toluene as immersion liquid.

The ultrasonic velocities were measured at a frequency of 4 MHZ, using pulse echo technique. The elapsed time between the initiation and the receipt of the pulse appearing on the screen of a flaw detector (USM3-Kraut-Kramer) was measured by standard electronic circuit PM 3055 Philips. The ultrasonic velocity was obtained by dividing the round trip distance by the elapsed time. The transducer was coupled to the specimen by an ultrasonic couplant, which proved to be very suitable for this purpose. The glass samples were irradiated using C_s^{137} γ-ray source at a dose rate of $24x10^{-2}$ Gy/min at 30 cm from the source at room temperature. The different doses of irradiation were achieved by exposing the sample to the source for different periods of time. The used γ-ray doses are 0.5, 1, 3, 5, 7 and 10 Gy.

Results and Discussion:

Table (1) complies the basic data obtained with the present series of experiments. Values of elastic moduli given in Table (1) were calculated according to the well known equations:

$$\text{Longitudinal modulus} \qquad L = \rho\, V^2{}_l$$
$$\text{Shear modulus} \qquad G = \rho\, V^2{}_s$$

where V_l is the longitudinal velocity and V_s is the shear velocity. Debye temperature θ_D was calculated according to the equation given by Alers [10].

$$\theta_D = 251.2\, V_m \frac{(nM)^{1/3}}{\rho}$$

where V_m is the mean ultrasonic velocity given by:

$$\frac{3}{V_m^3} = \frac{1}{V_m^3} + \frac{1}{V_s^3}$$

where n is the number of atoms in the chemical formula, M is the effective molecular mass, and ρ is the density of the glass. Debye temperature represents the temperature at which all modes of vibrations in solid are excited and its increase implies an increase in rigidity of the network and hence an increase in velocity. The variation of Debye temperature with irradiation dose (Table 1)

Table (1): Properties for sodium borate glasses of five compositions irradiated with different γ-ray doses.

Dose (Gy)	**Na_2O (mol%)**	**Density (kg/m^3)**	**Shear velocity (m/s)**	**Long. Elastic Modulus (GPa)**	**Shear Elasti Modulus (GPa)**	**Debye Temp. θ_D (K)**	**Softening Temp. T_s (K)**
	2.00	1887	2223	27.72	9.32	318.1	268.8
	5.00	1950	2359	32.26	10.85	340.4	305.4
0.0	10.40	2060	2610	41.71	14.03	381.4	380.0
	20.00	2217	3000	59.31	19.95	444.8	517.5
	27.00	2293	3269	72.85	24.50	486.4	628.7
	2.00		2326	30.34	10.21	332.9	294.3
	5.00		2370	32.56	10.95	341.3	308.2
0.5	10.40		2641	42.72	14.37	384.9	388.7
	20.00		3049	61.27	20.61	452.1	534.5
	27.00		3282	73.42	24.70	488.3	633.7
	2.00		2373	31.59	10.62	339.6	306.3
	5.00		2377	32.75	11.02	342.9	310.1
1.0	10.40		2668	43.59	14.66	389.7	397.1
	20.00		3073	62.33	20.96	455.9	543.7
	27.00		3304	74.41	25.04	491.7	642.7
	2.00		2398	32.24	10.85	343.2	312.8
	5.00		2431	34.27	11.53	350.8	324.4
3.0	10.40		2717	45.21	15.21	397.1	411.9
	20.00		3106	63.58	21.39	460.5	554.6
	27.00		3316	74.96	25.21	493.4	646.9
	2.00		2419	32.81	11.04	346.2	318.3
	5.00		2465	35.23	11.85	355.6	333.5
5.0	10.40		2818	48.63	16.36	411.8	443.0
	20.00		3124	64.32	21.64	463.2	561.1
	27.00		3328	75.49	25.40	495.2	651.6
	2.00		2448	33.60	11.31	350.3	326.0
	5.00		2486	35.83	12.05	358.7	361.3
7.0	10.40		2866	50.31	16.92	419.1	457.8
	20.00		3140	64.96	21.86	465.5	566.9
	27.00		3349	76.44	25.71	498.3	659.9
	2.00		2471	34.25	11.52	353.6	332.2
	5.00		2503	36.32	12.22	361.1	343.9
10.0	10.40		3003	55.21	18.58	438.8	507.1
	20.00		3210	67.92	22.85	475.9	592.4
	27.00		3385	78.09	26.26	503.5	673.7

showed an increase in θ_D for 10.4 mol % Na_2O, which is relatively more than in the other glass samples. This increase is possibly due to structural changes induced by γ-irradiation and hence the compactness in the network. Softening temperature T_s was calculated from the expression given by (17) as,

$$T_s = \frac{V_s^2 M}{C^2 n}$$

where V_s is the shear velocity, M is the effective molecular weight, C is a constant of proportionality and equals to 0.5074 x 10^5 cm s^{-1} $K^{-1/2}$. It can be seen that as the Na_2O increases, the physical parameters increase. The greater the microhardness implies great softening temperature.

It is quite clear that the effect on the physical properties of irradiating sodium borate glasses with γ-radiation is relatively weak. However, for glass sample with 10.4 mol% Na_2O, a remarkable increase in ultrasonic velocity and other physical properties is significant.

Figure (1) shows the relation between longitudinal ultrasonic velocity (V_l) and irradiation dose, in the range from 0 to 10 Gray. It is observed that, the rate of change of ultrasonic velocity with respect to irradiation dose is more noticeable in the glass sample with 10.4 mol% Na_2O than the other glass samples, where the slope of the straight line representing this relation is the largest one. Fig. (2) shows the relation between microhardness (H) and γ-irradiation dose for the investigated five glass samples. Microhardness was calculated according to the equation given by Kodama [6] in the form;

$$H = (1\text{-}2\ \sigma)\ Y/6\ (1+\sigma)$$

where σ is Poisson's ratio (σ =(L – 2G)/ 2(L –G)) and Y is Young's modulus (Y = G(3L-4G)/(L-G),where G is the shear modulus. The figure shows the same fetures as that observed in Fig. (1).

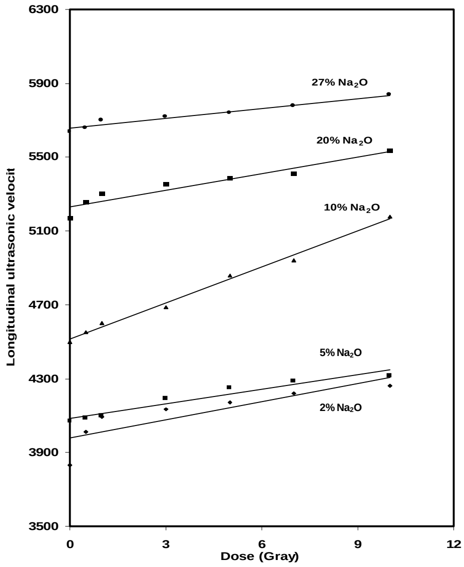

Fig. (1): Relation between longitudinal velocity and irradiation dose.

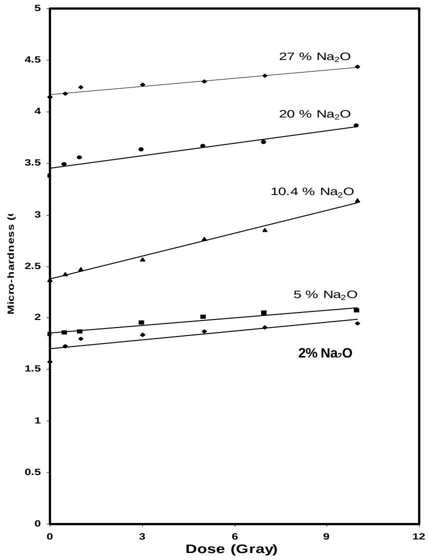

Fig. (2): Relation between Micro-hardness (H) and gamma irradiation dose.

The relations between the Young (Y) and bulk moduli (K = L – (4/3) G) of elasticity and γ-irradiation dose are shown in Figs. (3&4). Again, the rate of change of Young's or bulk moduli with respect to irradiation dose is more noticeable in the glass sample with 10.4 mol.% Na_2O content.

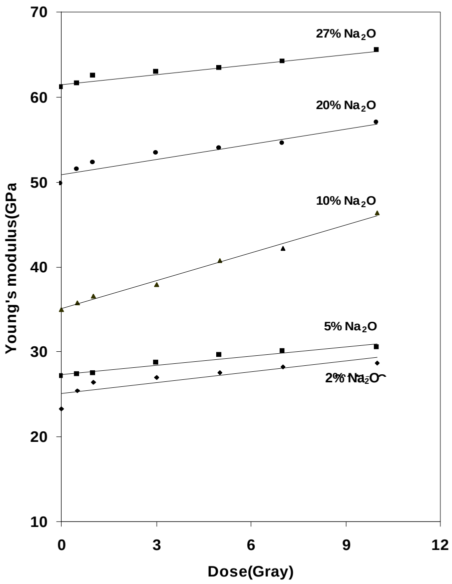

Fig.(3): Relation between Young's modulus and gamma irradiation dose.

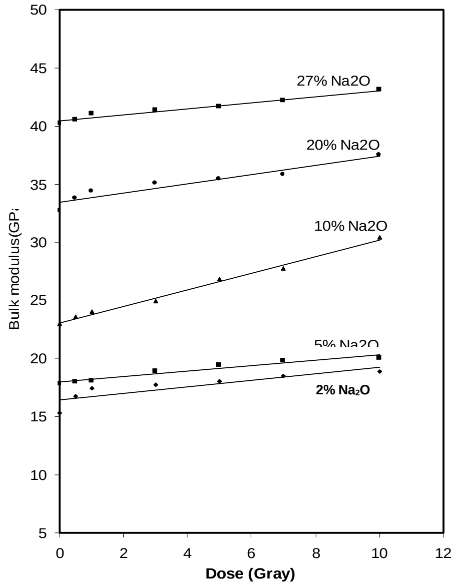

Fig. (4): Relation between bulk modulus and gamma irradiation dose.

The observed increase in ultrasonic velocity and all other physical properties of 10.4 mol% Na_2O content glass sample is merely related to structural changes of the network induced by γ-dose. According to Bisco and Warren [2], pure B_2O_3 exists in planner three-fold coordination. The addition of network modifier (Na_2O ions) produces four-fold coordinated boron by cross linking the planar triangles and would be expected to tighten and strengthen the network. Moreover, below 10.4 mol % Na_2O content, the boron atoms with coordination number three predominate and make B_2O_3 soft and easily deformed by stress. Above 10.4 mol.% Na_2O content, the boron atoms begin to change from three-fold to four-fold with coordination number of 4 [11]. This tetrahedral structure gives B_2O_3 maximum rigidity and increase in velocity indicating that the network former becomes rigid and resists deformation.

Moreover, it was reported that [12], with increasing Na_2O content, the first incorporation of alkali oxide leads to the coordination shift $[BO_3] \rightarrow [BO_4]$ with alkali ions adjoining the $[BO_4]$ tetrahedron. The structure is thus strengthened and consequently the velocity increased. This is because the number of points of linkage of polyhedrons rises from three to four. This is often located around 15 mol. % Na_2O content (10.4 in this study). Therefore, at this "critical composition", alkali borate glasses often exhibit borate anomaly.

Figure (5) depicts the relation between longitudinal ultrasonic velocity and sodium oxide content, for irradiated and non-irradiated two glass samples. It can be seen that the ultrasonic velocity increases rapidly with increasing Na_2O mol % content till about 10.4 mol % Na_2O. Above 10.4 and up to 27.0 mol.% Na_2O, a gradual increase in velocity is observed. The plot can be divided into two segments having different slopes. However, the increase in ultrasonic velocity indicates the gradual increase in rigidity and strengthening of the network continues up to 27.0 mol % Na_2O. The results obtained in the present study are in good agreement with the measurements of Gladkov and Tarasov [3], Kraus and Kurkjian [4] and Lorosch et al. [13].

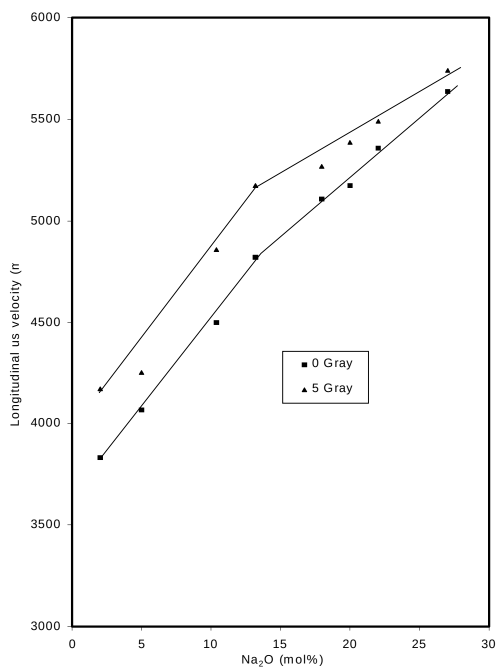

Fig. (5): Relation between longitudinal ultrasonic velocity and sodium oxide content

In the composition range 2.0 and 10.4 mol. % of Na_2O (first segment in Fig.(5), boron atoms change from three-fold to four-fold coordination of oxygen atoms by addition of modifier to form a three-dimensional connection of the network. This means that the glasses in this composition range are composed of soft B_2O_3 and hard Na_2O. This is most likely due to that the modifier is enclosed within the network in such a way that it prevents the deformation of the surrounding soft network.

At the critical composition of Na_2O = 10.4 mol %, alkali borate glasses often exhibit borate anomaly near this composition range [14]. The fact that the elastic modulus of B_2O_3 is maximal at this composition indicates that the borate network becomes rigid to high degree. Around 10.4 mol. % Na_2O, the three different species of boroxol ring, tetraborate group and diborate group, exist in large quantities at the same time [15]. It seems, therefore, that a combination of these borate groups forms the rigid network. Consequently, the degree to which the modifier prevents the deformation of the surrounding rigid network decreases.

In the composition range 10.4 - 27.0 mol % Na_2O, the boron atoms continue changing from the three-fold to the four-fold coordination of oxygen atoms. Replacing B_2O_3 (coordination number n_f =3, and cross link density n_c=1) by Na_2O (coordination number n_f. = 6 and cross link density n_c=4), the structure will be more linked and the resistance to the deformation by stress will be more strong. This leads to the increase in glass rigidity as evidenced by the increase in ultrasonic velocity.

Glass is considered as elastic substance and, thus, can be characterized through a modulus of elasticity. This modulus increases as the lengthening at a certain applied stress diminishes. That will be the case if the glass structure is rigid and therefore contains the fewest possible non bridging oxygen. When an alkali oxide is introduced to B_2O_3, the strengthen of the structure depends on the field strength of the cation. The relatively open structure of B_2O_3 glass makes its modulus of elasticity low. With increasing Na_2O content in the binary borate glass, the structure becomes more rigid and the modulus of elasticity increases. This increase is very pronounced and according to Takahashi [16], reaches the maximum value when the number of B atoms is the coordination number 4 has its maximum.

The relations between Young's modulus and microhardness and Na_2O mol % content are shown in Figs. [6 & 7), respectively. It is observed that the rate of change of Young's modulus or microhardness with respect to Na_2O content is not constant, but two different slopes can be observed in these plots.

The first in the range 2-10.4 mol % Na_2O and the second is in the range 10.4 - 27.0 mol % Na_2O.

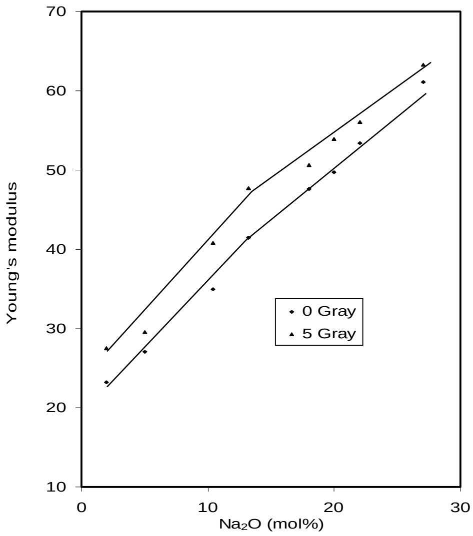

Fig.(6): Relation between Young's modulus and sodium oxide content.

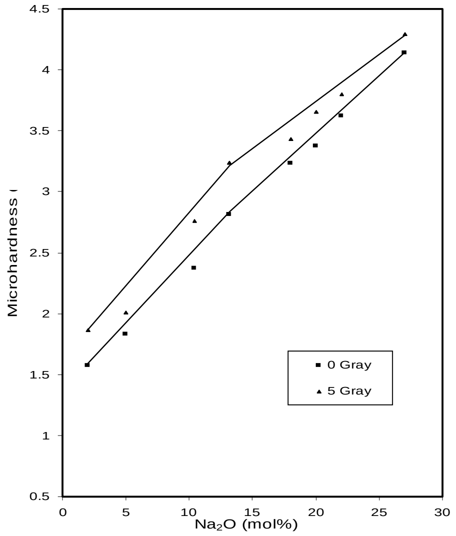

Fig. (7): Relation between microhardness and sodium oxide content.

Bulk modulus is the elastic property of glasses that can be derived most easily from the glass structure. B_2O_3 posses an open structure characterized by many open spaces. The addition of Na_2O will occupy such spaces and this should leads to an increase in bulk modulus. With low Na_2O contents, the bulk modulus is small since many open spaces are present which will be filled most quickly by the large Na^+ ions (ion radius of Na is 0.098 nm) so that the bulk modulus increases. With higher Na_2O contents, the ability for deformation of the cations becomes decisive. This is clear from Fig. (8), which shows the relation between bulk modulus and Na_2O mol %.

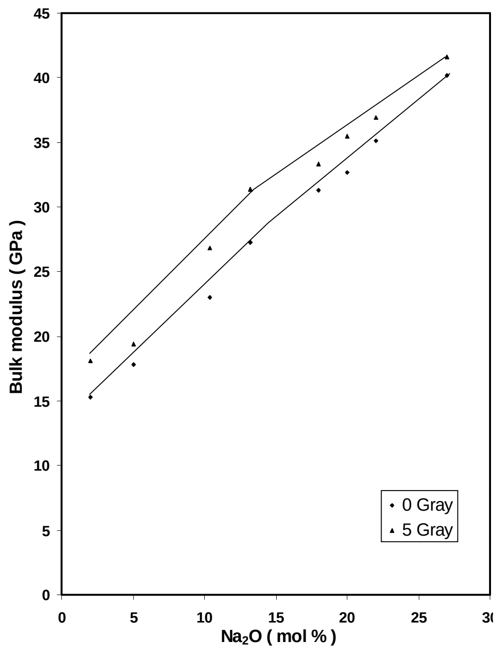

Fig. (8): Relation between bulk modulus and sodium oxide content.

Conclusion:

The above arguments allow to conclude that:

1. The effect of γ-irradiation on ultrasonic velocity in sodium borate glasses is not pronounced will the effect of sodium oxide content is more pronounced.

2. The composition range studied can be divided into three ranges:

   a) In the composition range from $2.0 < x < 10.40$ Na_2O mol.%, the increase in ultrasonic velocity is gradual due to the gradual increase in the rigidity of the glass and, hence, the strengthening of the network as a result of the gradual change of boron atoms from the three-fold to the four-fold coordination of oxygen atoms.

   b) At the composition of Na_2O=10.4 mol % (critical composition), three different species of boroxol ring, tetraborate group and diborate group exist in large quantities at the same time.

   c) In the composition range from $10.4 < x < 27.0$ Na_2O mol. %, the boron atoms continue changing from the three-fold to the four-fold coordination of oxygen atoms and ultrasonic velocity increases as the rigidity of the glass is increased.

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