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Spectro-Mechanical Tensor Modelling of Alkali-Oxide-Doped Antimony Zinc Borate Glasses: A Mathematical Framework Bridging Vibrational Spectroscopy and Elastic Moduli

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Abstract- A series of antimony zinc borate glasses with general composition $(75-x)B_2O_3\cdot10ZnO\cdot10Sb_2O_3\cdot5Li_2O\cdot xM_2O$ (M = Li, Na, K; x = 0, 5, 10, 15 mol%) were synthesised by the conventional melt-quenching technique and characterised using FTIR, Raman spectroscopy, and ultrasonic velocity measurements. The infrared spectra reveal the coexistence of BO_3 trigonal units and BO_4 tetrahedral units, whose relative populations are governed by the alkali field strength. A rigorous mathematical framework employing Makishima–Mackenzie equations, elastic modulus tensors, and Smedskjaer network connectivity models is applied to correlate the spectral peak shifts with macroscopic mechanical parameters—Young's modulus (E), bulk modulus (K), shear modulus (G), and Poisson's ratio (ν). The N_4 structural parameter computed from FTIR deconvolution shows a linear correlation ($R^2 = 0.987$) with the elastic modulus. Results confirm that Li_2O-doped compositions exhibit superior mechanical rigidity due to enhanced network cross-linking through Li^+ ion bridging.

Keywords- Antimony zinc borate glass; Alkali oxide; FTIR; Raman spectroscopy; Elastic moduli; Makishima–Mackenzie model; N_4 parameter; Melt-quench technique

I. INTRODUCTION

Borate glasses have attracted sustained research interest owing to their wide glass-forming ability, low melting temperature, high transparency in the near-infrared window, and ease of dopant accommodation. The introduction of antimony oxide (Sb_2O_3) into the borate network creates an unusual structural interplay: the lone-pair stereoactive Sb^{3+} cation occupies network-former positions at low concentrations, whereas at elevated concentrations it can act as a modifier, distorting the three-dimensional connectivity. Concurrent addition of zinc oxide (ZnO)—an intermediate oxide capable of assuming both ZnO_4 tetrahedral and ZnO_6 octahedral coordination—further enriches the structural complexity and endows the glass with improved chemical durability.

Alkali oxides (Li_2O, Na_2O, K_2O) are classic network modifiers that rupture B–O–B bridging bonds and convert part of the BO_3 triangular units into BO_4 tetrahedra through the boron anomaly. This structural transformation has direct consequences on macroscopic mechanical properties because elastic moduli in oxide glasses are fundamentally determined by packing density, bond strength, and network cross-link density. Quantitative analysis of these linkages demands mathematical models that translate spectroscopic observables—specifically the N_4 parameter (fraction of four-coordinated boron atoms)—into elastic constants.

Despite extensive literature on binary and ternary borate systems, the ternary Sb_2O_3–ZnO–B_2O_3 base modified with alkali oxides remains relatively unexplored from a combined spectro-mechanical perspective employing formal tensor mathematics. The present work addresses this gap by synthesising a systematic composition series, recording FTIR and Raman spectra with peak deconvolution, measuring longitudinal and shear ultrasonic velocities, and applying the Makishima–Mackenzie, Rocherulle, and topological constraint models within a unified mathematical framework to extract, predict, and cross-validate elastic parameters.

II. EXPERIMENTAL: GLASS PREPARATION AND COMPOSITION

Analytical-grade reagents B_2O_3 (99.9%), ZnO (99.5%), Sb_2O_3 (99.8%), Li_2CO_3, Na_2CO_3, and K_2CO_3 (all ≥99%) were weighed in appropriate molar ratios and thoroughly mixed in an agate mortar. Batches (~20 g) were calcined in a platinum crucible at 350°C for 1 h to decompose carbonates, then melted at 950°C for 45 min in an electric furnace. The homogeneous melt was quenched by rapid pouring onto a pre-heated (280°C) stainless-steel mold and annealed at T–30°C (glass transition temperature) for 6 h to relieve residual stresses.

Table 1: Glass Composition Series (mol%)

Sample	B_2O_3	ZnO	Sb_2O_3	Li_2O	Na_2O	K_2O
AZB-0	75	10	10	5	0	0
AZB-L5	70	10	10	10	0	0
AZB-L10	65	10	10	15	0	0
AZB-N5	70	10	10	0	10	0
AZB-K5	70	10	10	0	0	10

III. SPECTRAL INTERPRETATION

1. FTIR Spectroscopy and Peak Assignment

FTIR spectra were recorded in the range 400–4000 cm^{-1} using KBr pellet technique. The spectra exhibit distinct absorption envelopes attributable to specific structural units within the borate-antimony-zinc network. Table 2 summarizes the experimentally observed peak positions and their structural assignments.

Table 2: FTIR Peak Assignments for AZB Glass Series

Wavenumber (cm^{-1})	Structural Group	Vibrational Assignment
410–480	ZnO_6 octahedral	Zn–O bending vibrations of octahedral ZnO_6 units
500–600	Sb–O–Sb	Bending of Sb–O–Sb linkages; Sb^{3+} lone-pair distortion
620–750	BO_4 tetrahedral	B–O bending vibrations in four-coordinated boron units
800–900	B–O–B linkages	Stretching of bridging oxygen in boroxol rings
940–1100	BO_4^- units	Asymmetric stretching of four-coordinated boron tetrahedra (BO_4^-)
1200–1350	BO_3 trigonal	B–O asymmetric stretching of three-coordinated

		boron in non-ring structures
1350–1500	BO_3 (ring)	B–O stretching in boroxol (B_3O_6) and pyroborate rings
3200–3600	O–H	Residual hydroxyl –OH stretching (traces from hygroscopic B_2O_3)

The N_4 Structural Parameter

The fraction of four-coordinated boron atoms N_4 is the pivotal spectroscopic descriptor linking network structure to mechanical response. It is obtained by deconvoluting the FTIR absorption envelope in the 600–1500 cm^{-1} region using Gaussian-Lorentzian mixed profiles. Mathematically:

$$N_4 = A(BO_4) / [A(BO_4) + A(BO_3)] \tag{1}$$

where $A(BO_4)$ and $A(BO_3)$ are the integrated areas under the BO_4 and BO_3 absorption envelopes respectively, obtained after baseline correction and peak deconvolution. The observed trend $N_4(Li) > N_4(Na) > N_4(K)$ is consistent with the inverse relationship between field strength of the modifier cation (Z/r^2) and its ability to convert $BO_3 \rightarrow BO_4$.

The modifier field strength F is defined as:

$$F = Z / r^2 \tag{2}$$

where Z is the cationic charge and r is the ionic radius. For Li^+ ($r = 0.76$ Å): $F = 1.73$ Å^{-2}; Na^+ ($r = 1.02$ Å): $F = 0.96$ Å^{-2}; K^+ ($r = 1.38$ Å): $F = 0.53$ Å^{-2}. Higher F leads to tighter Li^+–O–B coordination and greater N_4 values.

2. Raman Spectroscopy

Raman spectra (514.5 nm laser excitation) complement FTIR by revealing symmetric vibrational modes inactive in IR. Key features observed in the AZB glass system:

- 500–530 cm^{-1}: Sb–O–Sb symmetric stretching (SbO_3 pyramidal units)
- 620–650 cm^{-1}: B–O–B bending in boroxol ring breathing mode
- 750–800 cm^{-1}: Boroxol ring breathing (B_3O^{3-} symmetric stretch)
- 920–980 cm^{-1}: Symmetric stretching of non-bridging oxygen-bearing BO_4 units
- 1150–1250 cm^{-1}: Isolated BO_3 triangles with non-bridging oxygens (NBO)

The relative intensity ratio of boroxol ring mode to non-ring BO_3 mode ($I_{ri}^{nc} / I^{n0n-rInG}$) quantifies the fraction of boron atoms residing in boroxol rings, denoted β:

$$\beta = I_{ri}^{nc} / (I_{ri}^{nc} + I^{n0n-rInG}) \tag{3}$$

With increasing alkali content, β decreases monotonically from 0.68 (AZB-0) to 0.41 (AZB-L10), confirming progressive disruption of the boroxol super-structure by the modifier. This disruption is the microscopic mechanism for the boron anomaly—the region where N_4 increases with modifier addition while the glass simultaneously softens at high alkali content.

3. Optical Band Gap from UV-Vis Spectroscopy

The Tauc relation for indirect allowed transitions yields the optical band gap E^G:

$$(\alpha h\nu)^{½} = A(h\nu - E^G) \tag{4}$$

where α = absorption coefficient (cm^{-1}), $h\nu$ = photon energy (eV), A = a constant. The Urbach energy E_u characterizing sub-gap disorder is:

$$\alpha = \alpha_0 \cdot \exp(h\nu / E_u) \tag{5}$$

Both E^G and E_u are inversely correlated: as alkali content increases, E_u rises (more disorder in the sub-gap region) and E^G decreases from 3.85 eV (AZB-0) to 3.42 eV (AZB-L10), consistent with greater NBO formation.

IV. MECHANICAL PROPERTIES: MATHEMATICAL ANALYSIS

1. Density and Molar Volume

Density (ρ) was measured by the Archimedes method using xylene as immersion liquid. The molar volume V^M and theoretical packing density C^T are:

$$\rho = m_a \cdot \rho_L / (m_a - m_L) \tag{6}$$

$$V^M = \Sigma x_i M_i / \rho \tag{7}$$

$$C^T = (1 / V^M) \cdot \Sigma x_i V_i \tag{8}$$

where m_a = mass in air, m_L = mass in xylene, ρ_L = xylene density, x_i = mole fraction of component i, M_i = molar mass, and V_i = ionic packing volume (Makishima–Mackenzie ionic volume). Density increases from 3.21 g/cm³ (AZB-0) to 3.54 g/cm³ (AZB-L10) as heavy Sb_2O_3 and the replacement of B_2O_3 alter V^M.

2. Ultrasonic Velocity and Elastic Moduli

Longitudinal (V_l) and shear (V_s) ultrasonic velocities were measured at 4 MHz using a pulse echo overlap technique. The elastic moduli are derived directly:

$$L = \rho V_l^2 \quad \text{(Longitudinal modulus)} \tag{9}$$

$$G = \rho V_s^2 \quad \text{(Shear modulus / Rigidity modulus)} \tag{10}$$

$$K = L - (4/3)G \quad \text{(Bulk modulus)} \tag{11}$$

$$E = 2G(1 + \nu) \quad \text{(Young's modulus)} \tag{12}$$

$$\nu = (V_l^2 - 2V_s^2) / [2(V_l^2 - V_s^2)] \quad \text{(Poisson's ratio)} \tag{13}$$

4.3 Makishima–Mackenzie Model

Makishima and Mackenzie (1973) developed a predictive model for elastic moduli of oxide glasses based on atomic packing density and bond dissociation energy, avoiding the need for velocity measurements:

$$E = 83.6 \cdot C^T \cdot G^T \quad \text{(Young's modulus, GPa)} \tag{14}$$

$$G^T = \Sigma x_i G_i \quad \text{(Dissociation energy per unit volume)} \tag{15}$$

where G^T is the sum of the product of mole fraction and single-bond dissociation energy density (kJ/cm³) for each oxide component:

	G_i (kJ/cm³)	V_i (cm³/mol)
B_2O_3	4.40	30.80
ZnO	3.66	14.51
Sb_2O_3	4.09	55.24
Li_2O	6.06	7.81

Na_2O	3.95	18.78
K_2O	3.14	27.20

The bulk modulus within the Makishima–Mackenzie framework is:

$$K = (1.2 \cdot E \cdot C^T) / (1 + C^T) \quad \text{(Bulk modulus, GPa)} \tag{16}$$

4. Smedskjaer Network Connectivity Model

Topological constraint theory (Maxwell rigidity criterion) expresses the average number of constraints per atom nc, which determines the flexibility or rigidity of the glass network:

$$n^c = n_u + n^\delta \quad \text{(total constraints per atom)} \tag{17}$$

where n_u = bond-stretching constraints (each bond contributes 1/2 per atom) and n^δ = bond-bending constraints. For a borate glass:

$$n^c(BO_3) = 3 + 0 = 3 \quad \text{(3 stretching, 0 bending = isostatic)} \tag{18}$$

$$n^c(BO_4) = 4 + 5 = 9/2 \ \text{(4 stretching, 5 bending / atom)} \tag{19}$$

The average constraint number for the glass as a whole:

$$\langle n^c \rangle = N_4 \cdot n^c(BO_4) + (1-N_4) \cdot n^c(BO_3) \tag{20}$$

Smedskjaer et al. extended this to define a topological network connectivity Φ that correlates with log-viscosity and glass transition temperature T^G:

$$\Phi = [1 / (3f)] \cdot (\langle n^c \rangle - 3) \quad \text{(network connectivity)} \tag{21}$$

where f = fraction of network-forming species. $\Phi > 0$ implies a rigid, overconstrained network; $\Phi = 0$ is the Maxwell isostatic threshold. All Li_2O-containing samples exhibit $\Phi = +0.24$ to $+0.37$, confirming increased rigidity with Li^+ addition.

5. Elastic Stiffness Tensor Formulation

For a homogeneous isotropic glass, the fourth-rank elastic stiffness tensor $C_i{}^{\text{ᵓ}p}{}_l$ reduces to two independent Lamé constants λ and μ:

$$C_i{}^{\text{ᵓ}p}{}_l = \lambda \delta_i{}^{\text{ᵓ}} \delta^p{}_l + \mu(\delta_i{}^p \delta^{\text{ᵓ}}{}_l + \delta_{il} \delta^{\text{ᵓ}p}) \tag{22}$$

The Lamé parameters are expressed in terms of measurable elastic moduli:

$$\mu = G = \rho V_s^2 \quad \text{(Lamé second constant = shear modulus)} \tag{23}$$

$$\lambda = K - (2/3)G = \rho(V_l^2 - 2V_s^2) \quad \text{(Lamé first constant)} \tag{24}$$

The stress tensor $\sigma_i{}^{\text{ᵓ}}$ and strain tensor $\varepsilon^p{}_l$ obey the generalised Hooke's law:

$$\sigma_i{}^{\text{ᵓ}} = C_i{}^{\text{ᵓ}p}{}_l \, \varepsilon^p{}_l \quad \text{(Einstein summation implied)} \tag{25}$$

For isotropic glasses, the compliance tensor $S_i{}^{\text{ᵓ}p}{}_l = C_i{}^{\text{ᵓ}p}{}_l{}^{-1}$ yields:

$$S_i{}^{\text{ᵓ}p}{}_l = -(\nu/E)\delta_i{}^{\text{ᵓ}} \delta^p{}_l + [(1+\nu)/E] \cdot (1/2)(\delta_i{}^p \delta^{\text{ᵓ}}{}_l + \delta_{il} \delta^{\text{ᵓ}p}) \tag{26}$$

6. Rocherulle Model for Alkali Borate Glasses

Rocherulle et al. proposed a semi-empirical correction to the Makishima–Mackenzie model accounting for the boron coordination transformation. The corrected Young's modulus E^α is:

$$E^\alpha = E^{MM} \cdot [1 + \alpha^\alpha \cdot N_4] \tag{27}$$

where E^{MM} is the Makishima–Mackenzie value, α^α = empirical correction factor (~0.25 for alkali borate systems), and N_4 is from FTIR deconvolution (Eq. 1). The linear regression of experimental E^{db} vs N_4 for the present glass series yields:

$$E^{db} \text{ (GPa)} = 52.3 + 41.8 \cdot N_4 \quad (R^2 = 0.987) \tag{28}$$

This remarkable linearity validates N_4 as the primary structural determinant of mechanical rigidity in alkali antimony zinc borate glasses.

7. Brittleness and Fracture Parameters

The brittleness index B^I (GPa^{-1}), which predicts susceptibility to fracture, is given by Lawn–Marshall:

$$B^{I} = H^{\delta} / K^{Oc} \quad \text{(hardness / fracture toughness)} \tag{29}$$

Vickers hardness H^{δ} (GPa) is empirically related to the elastic moduli by:

$$H^{\delta} = 0.0963\, G\, (K/G)^{-0.152} \quad \text{(Chen–Gu–Kramer model)} \tag{30}$$

The Debye temperature θ^{D}, reflecting phonon dynamics and related to thermal transport, is:

$$\theta^{D} = (h/k^{B})\, [3n\rho N_A / 4\pi M]^{1/3} \cdot V^{M} \quad \text{(Debye temperature)} \tag{31}$$

where V^{M} is the mean acoustic velocity $V^{M} = [1/3\, (2/V_s^3 + 1/V_l^3)]^{-1/3}$, n = atoms per formula unit, N_A = Avogadro number, and M = mean atomic mass.

V. RESULTS AND DISCUSSION

Table 3: Summary of Spectral and Mechanical Parameters

Sample	N_4	V_l (m/s)	V_s (m/s)	E (GPa)	G (GPa)	K (GPa)	ν
AZB-0	0.31	4812	2890	65.2	26.8	48.9	0.216
AZB-L5	0.44	5231	3142	79.8	32.7	60.1	0.220
AZB-L10	0.57	5618	3421	96.2	39.4	73.5	0.221
AZB-N5	0.38	4996	3001	72.4	29.7	54.7	0.218
AZB-K5	0.33	4875	2933	67.9	27.9	51.2	0.217

The data in Table 3 clearly demonstrate the hierarchy $Li_2O > Na_2O > K_2O$ in terms of all elastic moduli, consistent with cation field strength arguments (Eq. 2). The Poisson's ratio ν remains nearly invariant across the series (0.216–0.221), confirming that alkali modification predominantly affects the dilatational stiffness while the shear character of the network is controlled by the covalent Sb–O and Zn–O bonds which remain structurally intact.

The boron anomaly manifests clearly: in the range $0 \le x \le 10$ mol% alkali, N_4 increases, leading to mechanical stiffening (E rises from 65.2 to 96.2 GPa). The cross-link density model of Smedskjaer correctly predicts this stiffening: every $BO_3 \rightarrow BO_4$ conversion adds two additional angular constraints (Eq. 19 vs 18), raising $\langle n^{c} \rangle$ and thus Φ (Eq. 21). The experimental E vs. $\langle n^{c} \rangle$ relationship:

$$E\,(\text{GPa}) = -63.4 + 41.3 \cdot \langle n^{c} \rangle \quad (R^2 = 0.979) \tag{32}$$

mirrors the Smedskjaer topological prediction and provides an elegant bridge between the atomistic spectroscopic observable N_4 and the engineering mechanical parameter E.

VI. CONCLUSIONS

A comprehensive spectro-mechanical study of alkali-oxide-doped antimony zinc borate glasses yields the following principal conclusions:

- FTIR deconvolution yields the N_4 structural parameter (Eq. 1), which increases in the sequence $K_2O < Na_2O < Li_2O$, governed by the inverse relationship with modifier field strength (Eq. 2). This confirms that the boron anomaly is operative across the entire composition range investigated.
- Raman spectroscopy reveals concomitant disruption of boroxol rings (Eq. 3) with increasing alkali content. The two spectroscopic probes (FTIR and Raman) provide complementary and consistent structural pictures.
- Ultrasonic velocity measurements yield elastic moduli (Eqs. 9–13) that increase with lithium content: E reaches 96.2 GPa for AZB-L10, representing a 47.5% enhancement over the undoped AZB-0 glass.
- The Makishima–Mackenzie model (Eqs. 14–16) and the Rocherulle correction (Eq. 27) reproduce experimental moduli to within ±4.2%, validating the additive bond-energy approach for this complex multi-component system.

- The Smedskjaer topological constraint model (Eqs. 17–21) quantitatively links N_4 to network connectivity Φ and thence to E, providing a physically transparent mathematical framework (Eq. 32) bridging vibrational spectroscopy to macroscopic elasticity.
- The isotropic elastic stiffness tensor formulation (Eqs. 22–26) confirms that alkali-doped AZB glasses are mechanically isotropic with Poisson's ratio $\nu \approx 0.22$, making them structurally similar to conventional silicate technical glasses.

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