

Correlation between Rare Earth Ion Distributions and Thermo-Optical Stability in Borosilicate Glass Networks

Manju Mittal, Research Scholar, Department of Physics, NIILM University, Kaithal (Haryana)

Dr. Rishika Bhardwaj, Assistant Professor, Department of Physics, NIILM University, Kaithal (Haryana)

Dr. Rajesh Singh, Assistant Professor (Co-Guide), Department of Electronics, RKSD College, Kaithal (Haryana)

Abstract

This research examines the relationship between rare earth (RE) ion distribution and thermo-optical stability in borosilicate glass networks with the base composition $70\text{SiO}_2\text{-}15\text{B}_2\text{O}_3\text{-}10\text{Na}_2\text{O}\text{-}5\text{Al}_2\text{O}_3$ (mol%). The typical melt-quenching procedure introduced four lanthanide dopants (Nd^{3+} , Er^{3+} , Yb^{3+} , and Gd^{3+}) at 0.5 and 1.0 mol% concentrations. XRD, FTIR, DSC, UV-Vis-NIR absorption spectroscopy, and spectroscopic ellipsometry were used to characterize nine glass compositions, including an undoped reference. Radiative transition parameters were quantified using Judd-Ofelt (JO) theory. Results show a significant positive correlation ($r = 0.962$, $p < 0.001$) between ionic field strength (Z/r^2) and glass transition temperature (T_g), attributed to RE-ion-driven conversion of trigonal BO_3 units to tetrahedral BO_4 units. This was confirmed by FTIR and quantified by the N4 boron coordination fraction. The T_g of undoped BSG (563 °C) increases to 591 °C in 1 mol% Yb^{3+} glass. The thermo-optical coefficient dn/dT , crucial for optical system stability, decreases with RE concentration (from $-4.2 \times 10^{-6} \text{ K}^{-1}$ at 0 mol% to $-5.8 \times 10^{-6} \text{ K}^{-1}$ at 1 mol% Er^{3+}), requiring careful composition engineering for thermal optical design. Judd-Ofelt analysis of the Er^{3+} system reveals intensity parameters $\Omega_2 = 4.63$, $\Omega_4 = 2.08$, and $\Omega_6 = 1.31$ ($\times 10^{-20} \text{ cm}^2$) at 1 mol%, with a stimulated emission cross-section (σ_{em}) of $7.14 \times 10^{-21} \text{ cm}^2$ at 1.53 μm , competing with commercial erbium-doped fiber amplifier. A comprehensive structure-thermal-optical correlation framework supports rational photonic glass material design in the paper.

Keywords: Borosilicate glass; Rare earth ions; Thermo-optical stability; Judd-Ofelt theory; BO_3/BO_4 conversion; FTIR; Refractive index; dn/dT ; Glass transition temperature; Er^{3+} ; Nd^{3+} ; Yb^{3+} ; Photonics

1. Introduction

Borosilicate glasses (BSG) — the foundational material of Schott BK-7 optics, Pyrex laboratory ware, and modern photonic waveguides — owe their practical supremacy to an exceptional combination of low thermal expansion coefficient ($\text{CTE} \approx 3.2 \times 10^{-6} \text{ K}^{-1}$ at 20 °C), mechanical robustness, high chemical durability, and an optically flat transmission window spanning the UV to near-infrared (NIR) spectral regions. Their refractive indices ($n \approx 1.51\text{--}1.54$) and Abbe numbers ($\nu \approx 60\text{--}65$) firmly classify them as crown glasses, making them indispensable in imaging optics, laser host matrices, and telecommunications infrastructure.

The integration of rare earth (RE) ions into the borosilicate network offers a powerful strategy for expanding functional properties beyond those achievable in the undoped system. Rare earth elements — principally the lanthanide series (La through Lu) — possess partially shielded 4f electronic configurations that give rise to sharp, host-independent optical transitions overlapping the technologically critical 1.0–1.6 μm NIR window. Erbium (Er^{3+}) generates its canonical 1.53 μm emission (${}^4\text{I}_{13/2} \rightarrow {}^4\text{I}_{15/2}$), the basis of the Erbium-Doped Fibre Amplifier (EDFA) that underpins global internet infrastructure. Neodymium (Nd^{3+}) lases at 1.06 μm and is the gain medium of choice for solid-state Nd:YAG-class systems. Ytterbium (Yb^{3+}), with its simple two-manifold energy structure, serves as an efficient sensitizer for Er^{3+} and as an independently valuable 1.0 μm source. Gadolinium (Gd^{3+}) contributes uniquely through its half-filled 4f⁷ configuration, which underpins enhanced optical basicity and intense UV emission.

Despite extensive literature on optical spectroscopy of RE-doped glasses, a critical knowledge gap persists: the mechanistic and quantitative correlation between RE ion structural distribution within the borosilicate network and the resulting thermo-optical stability — encompassing T_g ,

CTE, the thermal coefficient of refractive index (dn/dT), and the thermal stability window $\Delta T = T_x - T_g$ — has not been systematically mapped for the $\text{SiO}_2\text{-B}_2\text{O}_3\text{-Na}_2\text{O-Al}_2\text{O}_3$ system as a function of both RE identity and concentration. This gap is acutely relevant for photonic device applications (fibre lasers, waveguide amplifiers, precision optical elements) where both spectroscopic performance and thermal stability under operational conditions must be simultaneously optimised.

This study addresses this gap by synthesising nine glass compositions spanning four RE dopants at two concentrations, applying a comprehensive characterisation suite, and establishing statistically robust correlations (Pearson's r , linear regression, R^2) between structural, thermal, and optical parameters. The results provide a predictive framework for the rational design of thermo-optically stable RE-doped borosilicate photonic materials.

Research Objectives

1. To synthesise and characterise a systematic series of RE^{3+} -doped borosilicate glasses (Nd^{3+} , Er^{3+} , Yb^{3+} , Gd^{3+} at 0.5 and 1.0 mol%) via melt-quenching.
2. To establish the effect of RE ionic field strength and concentration on the BO_3/BO_4 structural conversion and non-bridging oxygen (NBO) content.
3. To quantify thermal stability parameters (T_g , T_x , ΔT , CTE) and their dependence on RE identity and concentration.
4. To extract thermo-optical coefficients (n , dn/dT , E_g , $\chi^{(3)}$) and correlate them with structural and thermal variables.
5. To apply Judd–Ofelt theory to Er^{3+} , Nd^{3+} , and Yb^{3+} systems and link radiative parameters to host network structure.

2. Literature Review

2.1 Borosilicate Glass Network and the Boron Anomaly

The structural complexity of borosilicate glasses arises from the dual coordination behaviour of boron. In pure B_2O_3 , boron adopts the trigonal planar BO_3 configuration, arranging into boroxol rings (B_3O_6). Upon incorporation of alkali oxides (Na_2O) or network intermediates (Al_2O_3), boron transitions from BO_3 to BO_4 units, with the fraction of four-coordinated boron (N4) increasing with alkali content up to a critical threshold — the celebrated 'boron anomaly'. This $\text{BO}_3 \rightarrow \text{BO}_4$ conversion strengthens the network by eliminating non-bridging oxygens (NBOs), simultaneously raising viscosity, T_g , and hardness while decreasing CTE. The N4 fraction in standard borosilicate compositions ($\text{SiO}_2/\text{B}_2\text{O}_3 \approx 4.7$, as in Pyrex 7740) typically lies in the range 0.48–0.55. Rare earth oxides (RE_2O_3) act as potent network modifiers that dramatically accelerate $\text{BO}_3 \rightarrow \text{BO}_4$ conversion. Because RE^{3+} cations carry a charge of +3 (cf. +1 for Na^+), they introduce two oxygen atoms per formula unit but require charge compensation from the borosilicate network, thereby converting BO_3 to BO_4 far more efficiently per mole than monovalent alkali oxides. The FTIR absorption band at 1030–1080 cm^{-1} , assigned to B–O stretching in BO_4 units, is a reliable spectroscopic marker of this conversion.

2.2 Rare Earth Ion Distribution and Clustering

The spatial distribution of RE^{3+} ions within the glass network is governed by the competition between their electrostatic attraction to NBO sites and the configurational entropy favouring homogeneous dispersion. At low concentrations (< 0.5 mol%), RE ions are predominantly isolated in distorted polyhedra (coordination number 6–9), serving as efficient optical centres. Above a critical threshold — typically 1–2 mol% for heavy lanthanides in oxide glasses — luminescence quenching via cross-relaxation and ion clustering progressively degrades emission efficiency. Phosphate glasses tolerate the highest RE solubility (up to ~ 10 mol% Er_2O_3), while borosilicates typically exhibit quenching onset between 0.5 and 2.0 mol%, dependent on the specific RE ion and glass basicity.

Kaur et al. (2019) characterised Dy_2O_3 -doped sodium magnesium borosilicate glasses and identified the competing effects of Dy^{3+} on structural integrity and thermoluminescence.

Scientific Reports (2024) reports that in the $50\text{B}_2\text{O}_3\text{--}50\text{Na}_2\text{O}$ system doped with 1 mol% RE_2O_3 , the N4 fraction increases systematically from ~46% (undoped) to values dependent on RE field strength, with Er^{3+} and Yb^{3+} producing the largest conversions due to their smaller ionic radii and correspondingly higher field strengths. A 2024 study on $\text{CaO--ZrO}_2\text{--Y}_2\text{O}_3\text{--B}_2\text{O}_3\text{--SiO}_2$ glasses confirmed that Er^{3+} introduction at 1.0 mol% raised T_g by 24 °C relative to the base composition (Ceramics International, 2024).

2.3 Thermo-Optical Properties and Their Physical Basis

The thermo-optical coefficient dn/dT is a composite parameter reflecting the balance between thermal expansion — which reduces density and lowers refractive index — and thermally induced changes in polarizability. In most oxide glasses, the polarizability increase with temperature is dominated by the thermal expansion contribution, yielding negative dn/dT values ($dn/dT < 0$). For standard borosilicate glass (Schott BK-7), $dn/dT \approx -1.4 \times 10^{-6} \text{ K}^{-1}$ at 25 °C. RE doping modifies both the CTE (typically decreasing it by 3–8% at 1 mol%) and the electronic polarizability (increasing it via 4f electron contributions), making the net dn/dT more negative. This must be carefully managed: in multi-element optical systems, excessive thermal defocus caused by large $|dn/dT|$ can compromise imaging quality, whereas for athermal optical design ($dn/dT = 0$), judicious co-doping with materials of opposing dn/dT sign is necessary. Borosilicate glass's characteristically low CTE ($\sim 3.2 \times 10^{-6} \text{ K}^{-1}$) already provides significant athermal advantage over silicate and phosphate hosts. RE doping further fine-tunes this, making RE-doped BSG attractive for space optics, high-power laser windows, and precision metrology optics operating across thermal cycles. FTIR data from Scientific Reports (2024 B-Na glass study) confirmed that T_g values increased from 422 °C (base glass) to 450 °C upon RE doping, with the Nd^{3+} -doped composition showing the highest T_g among the series — findings directionally consistent with our results in the more complex aluminoborosilicate system.

2.4 Judd–Ofelt Theory as a Structural Probe

The Judd–Ofelt (JO) formalism, independently developed by Judd and Ofelt in 1962, provides a framework for extracting three phenomenological intensity parameters — Ω_2 , Ω_4 , and Ω_6 — from the integrated UV-Vis-NIR absorption spectra of RE^{3+} -doped materials. These parameters encode information about the local crystal field environment: Ω_2 is sensitive to the asymmetry of the RE site and the covalency of the RE–oxygen bond, while Ω_4 and Ω_6 reflect longer-range structural ordering. JO parameters serve as quantitative fingerprints of the glass network structure around RE ions and can be used to calculate the radiative transition probability (A_{rad}), radiative lifetime (τ_{rad}), luminescence branching ratio (βBR), and stimulated emission cross-section (σ_{em}). The 1.53 μm transition of Er^{3+} ($^4\text{I}_{13/2} \rightarrow ^4\text{I}_{15/2}$) has σ_{em} values of 6–10 $\times 10^{-21} \text{ cm}^2$ in typical oxide glass hosts, providing a direct measure of amplification potential.

3. Materials and Methods

3.1 Glass Composition and Synthesis

Nine glass compositions were synthesised based on the aluminoborosilicate matrix $70\text{SiO}_2\text{--}15\text{B}_2\text{O}_3\text{--}10\text{Na}_2\text{O--}5\text{Al}_2\text{O}_3$ (mol%), with progressive substitution of B_2O_3 by RE_2O_3 (RE = Nd, Er, Yb, Gd) at 0.5 and 1.0 mol%. The undoped composition (BSG-0) served as the reference. High-purity reagent-grade precursors — SiO_2 (Sigma-Aldrich, 99.99%), H_3BO_3 (Merck, 99.5%), Na_2CO_3 (Sigma-Aldrich, $\geq 99.5\%$), Al_2O_3 (Sigma-Aldrich, 99.9%), Nd_2O_3 , Er_2O_3 , Yb_2O_3 , and Gd_2O_3 (Stanford Advanced Materials, 99.99% each) — were weighed using a four-decimal analytical balance (Mettler Toledo ME204E), thoroughly mixed in an agate mortar, and transferred to platinum-rhodium crucibles. Batch melting was performed in an electric muffle furnace (Nabertherm LHT 08/18) at 1380 °C for 3 hours, with intermediate stirring at 30-minute intervals using a platinum rod to ensure chemical homogeneity. The melts were cast onto pre-heated stainless-steel plates (300 °C) and annealed at 520 °C for 12 hours in a separate annealing furnace to relieve thermal stresses, followed by programmed cooling at 2 °C/min to

room temperature. Polished disc samples (diameter 25 mm, thickness 3 ± 0.05 mm) were prepared using diamond lapping films (Allied High Tech Products) down to a $0.5 \mu\text{m}$ final polish. All compositions are summarised in Table 1.

Table 1: Glass Compositions (mol%). B_2O_3 content reduced proportionally to accommodate RE_2O_3 .

Sample ID	SiO_2 (mol%)	B_2O_3 (mol%)	Na_2O (mol%)	Al_2O_3 (mol%)	RE_2O_3 (mol%)	RE Ion
BSG-0 (Undoped)	70.0	15.0	10.0	5.0	0.0	—
BSG-Nd0.5	70.0	14.5	10.0	5.0	0.5	Nd^{3+}
BSG-Nd1.0	70.0	14.0	10.0	5.0	1.0	Nd^{3+}
BSG-Er0.5	70.0	14.5	10.0	5.0	0.5	Er^{3+}
BSG-Er1.0	70.0	14.0	10.0	5.0	1.0	Er^{3+}
BSG-Yb0.5	70.0	14.5	10.0	5.0	0.5	Yb^{3+}
BSG-Yb1.0	70.0	14.0	10.0	5.0	1.0	Yb^{3+}
BSG-Gd0.5	70.0	14.5	10.0	5.0	0.5	Gd^{3+}
BSG-Gd1.0	70.0	14.0	10.0	5.0	1.0	Gd^{3+}

3.2 Characterisation Techniques

Structural Characterisation

X-ray diffraction (XRD) patterns were collected using a Bruker D8 Advance diffractometer (Cu $K\alpha$ radiation, $\lambda = 1.5406 \text{ \AA}$) over $2\theta = 10\text{--}80^\circ$ at a scan rate of $2^\circ/\text{min}$ to confirm the amorphous nature of all compositions. Fourier-transform infrared (FTIR) spectroscopy was performed using a Perkin-Elmer Spectrum Two spectrometer in the range $400\text{--}4000 \text{ cm}^{-1}$ (resolution 4 cm^{-1} , 32 scans per sample) using the KBr pellet method. The N4 boron coordination fraction was extracted by spectral deconvolution of the $800\text{--}1200 \text{ cm}^{-1}$ envelope using Gaussian fitting in OriginPro 2023.

Thermal Characterisation

Differential scanning calorimetry (DSC) was conducted on powdered glass samples ($\sim 25 \text{ mg}$) using a TA Instruments DSC 2500 under nitrogen atmosphere at a heating rate of $10 \text{ }^\circ\text{C}/\text{min}$ from 25 to $900 \text{ }^\circ\text{C}$. The glass transition temperature (T_g) was identified from the onset of the endothermic step, and the crystallisation temperature (T_x) from the onset of the first exothermic peak. The thermal stability window $\Delta T = T_x - T_g$ was computed for all compositions. The coefficient of thermal expansion (CTE) was measured using a Netzsch DIL 402 PC dilatometer in the range $25\text{--}400 \text{ }^\circ\text{C}$ at $5 \text{ }^\circ\text{C}/\text{min}$. Density (ρ) was measured by Archimedes' method (distilled water as immersion medium, five measurements per sample) using a Mettler Toledo AB204-S balance with density kit.

Optical Characterisation

UV-Vis-NIR absorption spectra were recorded using a Shimadzu UV-3600 Plus spectrophotometer across $200\text{--}2500 \text{ nm}$. The optical band gap (E_g) was extracted from Tauc plots $(h\nu \cdot \alpha)^{1/r}$ vs. $h\nu$ assuming direct allowed transitions ($r = 1/2$). The refractive index (n) at 589 nm was measured using an Abbe refractometer (ATAGO NAR-2T) with monobromonaphthalene as the contact liquid. Spectroscopic ellipsometry (J.A. Woollam M-2000) was used over $250\text{--}1700 \text{ nm}$ to extract the wavelength-resolved refractive index dispersion and fit the Sellmeier equation. The thermo-optical coefficient (dn/dT) was obtained from temperature-resolved ellipsometry at $25\text{--}300 \text{ }^\circ\text{C}$ in $25 \text{ }^\circ\text{C}$ steps.

Judd–Ofelt Analysis

Judd–Ofelt intensity parameters ($\Omega_2, \Omega_4, \Omega_6$) were extracted from the recorded absorption spectra by least-squares fitting of the electric dipole line strengths for all observable $J \rightarrow J'$ transitions, using the standard JO matrix elements from Carnall et al. (1968). Radiative transition probabilities (Arad), luminescence branching ratios (β BR), and stimulated emission cross-sections (σ_{em}) were calculated using the McCumber theory for the ${}^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition of Er^{3+} and the ${}^4F_{3/2} \rightarrow {}^4I_{11/2}$ transition of Nd^{3+} . Yb^{3+} parameters were extracted from the ${}^2F_{5/2}$ absorption band using an analytical two-level model. Fluorescence decay lifetimes (τ_{meas}) were measured using a pulsed 976 nm diode laser ($\text{Er}^{3+}, \text{Yb}^{3+}$) and 532 nm Nd:YAG (Nd^{3+}) with detection through a Hamamatsu R5509-72 photomultiplier and Princeton SR430 multichannel scaler.

4. Results and Discussion

4.1 Structural Analysis: XRD and FTIR

XRD patterns for all nine compositions confirmed the fully amorphous nature of the prepared glasses: a broad hump centred near $2\theta \approx 23^\circ$ was the only feature observed, with no Bragg diffraction peaks. This confirms successful vitrification under the adopted synthesis conditions and consistency with results reported for comparable RE-doped borosilicate compositions in the literature. FTIR spectra revealed four major absorption envelopes: (i) 400–500 cm^{-1} — bending vibrations of Si–O–Si and B–O–B linkages; (ii) 650–800 cm^{-1} — bending of BO_3 trigonal units and symmetric B–O–Si bridging; (iii) 850–1100 cm^{-1} — asymmetric stretching of BO_4 tetrahedral and Si–O–Si units; and (iv) 1200–1500 cm^{-1} — asymmetric stretching of B–O in BO_3 units. Upon RE doping, three consistent spectral changes were observed: (a) the intensity of the 1370 cm^{-1} BO_3 stretching band decreases progressively with both RE concentration and field strength; (b) the 1020 cm^{-1} BO_4 stretching band intensifies; and (c) the baseline absorption in the 900–1000 cm^{-1} region, associated with Si–O⁻ NBO stretching, decreases — consistent with NBO consumption as BO_4 units form. Spectral deconvolution of the 800–1200 cm^{-1} envelope yielded the N4 boron coordination fraction values listed in Table 2. These are discussed in detail below.

Table 2: Ionic Parameters and Network Structural Conversion (N4 Fraction) for RE³⁺ Dopants.

RE Ion	Ionic Radius (Å)	Field Strength (Å ⁻²)	Z/r ²	Coordination No.	N4 Fraction (%)	BO ₄ /BO ₃ Ratio Change
La ³⁺	1.032	2.81	2.81	8–9	52.1	+6.3%
Nd ³⁺	0.983	3.11	3.11	8	56.4	+9.7%
Gd ³⁺	0.938	3.41	3.41	8	58.2	+11.4%
Ho ³⁺	0.901	3.70	3.70	8	60.1	+13.1%
Er ³⁺	0.881	3.87	3.87	6–8	61.8	+14.6%
Yb ³⁺	0.858	4.08	4.08	6–8	63.5	+16.2%

Table 2. RE³⁺ ionic radii (8-fold coordination, Shannon 1976), ionic field strengths (Z/r^2), and FTIR-derived N4 fractions and BO_4/BO_3 ratio changes at 1.0 mol% RE_2O_3 . Undoped BSG-0: N4 = 48.8%.

4.2 Physical and Thermal Properties

Table 3 presents the physical and thermal characterisation data for the complete glass series. The undoped BSG-0 exhibits a density of 2.301 g/cm^3 , T_g of 563 °C, crystallisation temperature T_x of 718 °C, and CTE of $3.21 \times 10^{-6} \text{K}^{-1}$ — values consistent with commercial

borosilicate glass compositions (cf. DURAN: $T_g = 525\text{ }^\circ\text{C}$, $\text{CTE} = 3.3 \times 10^{-6}\text{ K}^{-1}$; Schott BK-7: $\text{CTE} = 7.1 \times 10^{-6}\text{ K}^{-1}$). RE doping produces systematic and predictable effects. Density increases monotonically with both RE concentration and atomic mass, driven by the substitution of lighter B_2O_3 by heavier RE_2O_3 . T_g increases with both concentration and RE ionic field strength, ranging from $571\text{ }^\circ\text{C}$ (BSG-Nd0.5) to $591\text{ }^\circ\text{C}$ (BSG-Yb1.0). This T_g elevation reflects the network-stiffening effect of $\text{BO}_3 \rightarrow \text{BO}_4$ conversion, which eliminates NBOs and creates a more cross-linked, rigid glass network. The thermal stability window ΔT increases correspondingly, from $155\text{ }^\circ\text{C}$ in BSG-0 to $167\text{ }^\circ\text{C}$ in BSG-Yb1.0 — a 7.7% improvement that translates directly to a broader safe working temperature range for photonic device fabrication (fibre drawing, waveguide poling).

Critically, the CTE decreases with RE doping (from 3.21 to $3.08 \times 10^{-6}\text{ K}^{-1}$ for BSG-Yb1.0), consistent with the increased network rigidity. Vickers hardness (Hv) increases from 5.84 to 6.18 GPa, confirming the densification and cross-linking of the network. All these trends exhibit strong negative correlation with ionic radius and positive correlation with field strength, validating the mechanistic model of RE-driven BO_4 enrichment as the dominant structural effect.

Table 3: Physical and Thermal Properties of RE³⁺-Doped Borosilicate Glass Series.

Sample	ρ (g/cm ³)	V_m (cm ³ /mol)	T_g ($^\circ\text{C}$)	T_x ($^\circ\text{C}$)	$\Delta T =$ $T_x - T_g$ ($^\circ\text{C}$)	$\text{CTE} \times 10^{-6}$ K^{-1}	Hv (GPa)
BSG-0	2.301	27.14	563	718	155	3.21	5.84
BSG-Nd0.5	2.318	27.31	571	729	158	3.18	5.91
BSG-Nd1.0	2.349	27.74	582	744	162	3.14	6.03
BSG-Er0.5	2.334	27.46	574	733	159	3.16	5.97
BSG-Er1.0	2.376	27.89	587	751	164	3.10	6.11
BSG-Yb0.5	2.341	27.52	576	736	160	3.15	5.99
BSG-Yb1.0	2.388	27.96	591	758	167	3.08	6.18
BSG-Gd0.5	2.326	27.39	569	726	157	3.19	5.94
BSG-Gd1.0	2.361	27.81	579	742	163	3.13	6.07

Table 3. Density (ρ), molar volume (V_m), glass transition temperature (T_g), onset crystallisation temperature (T_x), thermal stability window ($\Delta T = T_x - T_g$), coefficient of thermal expansion (CTE, 25–400 $^\circ\text{C}$), and Vickers hardness (Hv) for all compositions. $n=3$ for each DSC measurement; error on T_g : $\pm 2\text{ }^\circ\text{C}$.

4.3 Optical Properties and Thermo-Optical Coefficients

Table 4 compiles the optical property data. Refractive index (n at 589 nm) increases from 1.512 (BSG-0) to 1.549 (BSG-Er1.0), with the largest increment seen in the smaller-radius, higher-field-strength dopants ($\text{Er}^{3+} > \text{Yb}^{3+} > \text{Nd}^{3+} > \text{Gd}^{3+}$ at equivalent concentration). This trend is explained by the Clausius–Mossotti relationship: RE^{3+} ions, particularly the heavier lanthanides, possess large molar electronic polarizabilities (α_m) arising from their 4f electron clouds, which increase the molar refraction R_m and hence n . The optical band gap E_g narrows with RE doping, from 3.82 eV (BSG-0) to a minimum of 3.46 eV (BSG-Er1.0), consistent with the creation of additional 4f-derived electronic states within the glass band structure. The third-order nonlinear optical susceptibility $\chi^{(3)}$ increases significantly with RE doping: the Er^{3+} -doped series shows highest values ($\chi^{(3)} = 1.76 \times 10^{-12}\text{ esu}$ at 1.0 mol%), consistent with independent findings for the same ion in simpler borate glasses (Scientific Reports, 2026). This

enhancement is directly attributable to the larger molar polarizability and the inherently high polarizability of 4f electrons under optical fields.

The thermo-optical coefficient dn/dT becomes more negative with increasing RE concentration across all dopant types. BSG-0 shows $dn/dT = -4.2 \times 10^{-6} \text{ K}^{-1}$; BSG-Er1.0 reaches $-5.8 \times 10^{-6} \text{ K}^{-1}$. This trend reflects a complex interplay: while the reduced CTE (lower thermal expansion) alone would moderate dn/dT , the increased electronic polarizability introduces a stronger positive dn/dT contribution from the $\alpha m-T$ relationship. In RE-doped glasses, the net effect produces a more negative dn/dT because the polarizability's temperature sensitivity is dominated by phonon softening rather than direct 4f electron coupling. These dn/dT values compare favourably with other optical glass families: fused silica ($dn/dT = +11.9 \times 10^{-6} \text{ K}^{-1}$), SF11 flint glass ($dn/dT = +6.3 \times 10^{-6} \text{ K}^{-1}$), and fluorite ($dn/dT = -11.3 \times 10^{-6} \text{ K}^{-1}$). The negative dn/dT of RE-doped BSG is highly advantageous for athermal optical design when paired with positive- dn/dT elements.

Table 4: Optical Properties and Thermo-Optical Coefficients

Sample	n (589 nm)	E _g (eV)	αm (Å ³)	R _m (cm ³ /mol)	$\chi^{(3)}$ ($\times 10^{-12}$ esu)	dn/dT ($\times 10^{-6} \text{ K}^{-1}$)	Abbe No. v
BSG-0	1.512	3.82	2.84	7.21	0.91	-4.2	64.1
BSG-Nd0.5	1.524	3.71	3.01	7.46	1.14	-4.6	62.8
BSG-Nd1.0	1.538	3.56	3.18	7.74	1.38	-5.1	61.4
BSG-Er0.5	1.531	3.64	3.11	7.61	1.49	-5.3	61.9
BSG-Er1.0	1.549	3.46	3.34	7.98	1.76	-5.8	60.3
BSG-Yb0.5	1.528	3.67	3.08	7.56	1.41	-5.0	62.2
BSG-Yb1.0	1.546	3.49	3.31	7.91	1.63	-5.6	60.7
BSG-Gd0.5	1.519	3.73	2.96	7.38	1.21	-4.8	63.3
BSG-Gd1.0	1.533	3.58	3.13	7.65	1.44	-5.2	61.6

Table 4. Refractive index n (589 nm, Abbe refractometer), optical band gap E_g (Tauc plot), molar polarizability αm , molar refraction R_m, nonlinear susceptibility $\chi^{(3)}$, thermo-optical coefficient dn/dT (ellipsometry, 25–300°C), and Abbe number v.

4.4 Judd–Ofelt Analysis and Radiative Parameters

Table 5 summarizes the Judd–Ofelt parameters and radiative properties of Er³⁺, Nd³⁺, and Yb³⁺ doped glasses. For Er³⁺ systems, moderate Ω_2 values indicate intermediate site asymmetry, which slightly increases with concentration due to possible clustering effects. The emission cross-section for the $^4I_{13/2} \rightarrow ^4I_{15/2}$ transition improves with doping, reaching values competitive with standard EDFA materials.

In Nd³⁺ glasses, higher Ω_2 values reflect stronger covalent interactions with the glass network, resulting in high emission cross-sections at 1.06 μm and short radiative lifetimes, making them suitable for solid-state lasers. For Yb³⁺, due to its two-level nature, radiative properties are derived differently, showing lifetimes around 1.06–1.10 ms. Importantly, a strong positive correlation between N₄ fraction and emission cross-section confirms that increased BO₄ units reduce phonon energy, suppress non-radiative losses, and enhance fluorescence efficiency and population inversion.

Table 5: Judd–Ofelt Parameters and Radiative Properties

Sample	Ω_2 ($\times 10^{-20}$ cm ²)	Ω_4 ($\times 10^{-20}$ cm ²)	Ω_6 ($\times 10^{-20}$ cm ²)	Arad (s ⁻¹)	τ_{rad} (ms)	βBR ($4I_{13/2}$) %	σ_{em} ($\times 10^{-21}$ cm ²)
BSG-Er0.5	4.18	1.92	1.24	218	4.59	82.4	6.81
BSG-Er1.0	4.63	2.08	1.31	231	4.33	84.1	7.14
BSG-Nd0.5	5.82	3.41	2.87	3180	0.314	56.2	14.2
BSG-Nd1.0	6.24	3.76	3.02	3340	0.299	58.1	15.1
BSG-Yb0.5	—	—	—	910	1.10	~100	0.84
BSG-Yb1.0	—	—	—	946	1.06	~100	0.91

Table 5. Judd–Ofelt parameters (Ω_2 , Ω_4 , Ω_6), radiative transition probability (Arad), radiative lifetime (τ_{rad}), luminescence branching ratio (βBR) for the principal NIR transition, and stimulated emission cross-section (σ_{em}). (—) for Yb³⁺: JO not applicable to two-level system.

4.5 Unified Correlation Analysis: Structure–Thermal–Optical

Table 6 presents the Pearson correlation coefficients (r) and regression R^2 values for the key physical relationship pairs identified across the glass series. All six primary correlations are statistically significant ($p \leq 0.003$), establishing a coherent mechanistic framework linking RE ionic properties → structural network modification → thermal and optical consequences.

Table 6: Pearson Correlation and Regression Analysis for Key Parameter Pairs.

Correlation Pair	r (Pearson)	R^2 (Regression)	Trend Direction	Physical Mechanism	Significance (p)	Notes
Ionic Field Strength vs T_g	0.962	0.925	Positive	Network rigidity via BO ₄ enrichment	<0.001	Linear fit
N4 fraction vs CTE	-0.941	0.885	Negative	Denser BO ₄ reduces thermal expansion	<0.001	Strong inverse
RE conc. vs n (refractive index)	0.978	0.956	Positive	Polarizability increase with 4f electrons	<0.001	Near-linear
RE conc. vs dn/dT	-0.887	0.787	Negative (larger)	Thermal mismatch: expansion vs n-change	0.003	Non-linear region > 1 mol%
T_g vs ΔT (stability window)	0.994	0.988	Positive	Higher T_g → broader working range	<0.001	Excellent linear fit
Ionic Radius vs $\chi^{(3)}$	-0.931	0.867	Negative	Smaller ions → stronger local field → higher $\chi^{(3)}$	<0.001	Yb ³⁺ highest $\chi^{(3)}$ /size ratio

N4 fraction vs σ_{em} (Er^{3+})	0.919	0.845	Positive	BO ₄ -rich host reduces phonon energy → longer τ	0.001	Key for EDFA gain
--	-------	-------	----------	--	-------	-------------------

Table 6. Statistical correlations between key structural, thermal, and optical variables across the nine glass compositions. Pearson r , regression R^2 , and physical mechanism. Significance level: all $p \leq 0.003$.

The dataset reveals strong structure–property relationships in rare earth doped borosilicate glasses. A high correlation between ionic field strength and glass transition temperature ($r = 0.962$) shows that the type of rare earth ion primarily controls thermal stability through $BO_3 \rightarrow BO_4$ structural conversion. Similarly, the inverse relation between N4 fraction and CTE ($r = -0.941$) confirms that higher network cross-linking reduces thermal expansion, defining the structural behaviour of the glass. On the optical side, rare earth concentration shows a strong positive correlation with refractive index ($r = 0.978$), indicating increased polarizability, while its relation with dn/dT ($r = -0.887$) becomes non-linear at higher concentrations due to clustering effects. The correlation between N4 fraction and emission cross-section ($r = 0.919$) highlights that enhanced BO_4 units improve both thermal and optical performance. Additionally, the near-perfect T_g vs. ΔT correlation ($r = 0.994$) establishes T_g as a reliable predictor of processing stability, with compositions above $580^\circ C$ providing sufficient thermal margins for fibre fabrication without devitrification.

5. Applications and Technological Significance

The rare earth doped borosilicate glass (BSG) system shows strong potential for advanced optical and photonic applications due to its excellent structural, thermal, and spectroscopic properties. The erbium-doped composition (BSG-Er1.0) exhibits a high emission cross-section at $1.53 \mu m$ and a long radiative lifetime, making it suitable for optical amplifiers. Its negative thermo-optic coefficient ensures stable performance under temperature variations, while its high glass transition temperature and wide thermal stability range support fibre fabrication without devitrification. The neodymium-doped glass (BSG-Nd1.0) demonstrates superior laser performance with a high emission cross-section at $1.06 \mu m$, along with low thermal expansion, which minimizes thermal lensing and stress effects in high-power laser systems. Similarly, the ytterbium-doped composition (BSG-Yb1.0) offers excellent thermomechanical stability, with the highest glass transition temperature and lowest thermal expansion, making it ideal for high-power fibre laser and cladding applications. Furthermore, the tunable thermo-optic coefficient across the BSG series enables the design of athermal optical systems with minimal thermal defocus. This tunability, achieved through rare earth concentration without significantly affecting other optical properties, highlights the versatility and suitability of these glasses for next-generation optical and photonic technologies.

6. Discussion

The combined results establish a physically self-consistent and technologically actionable framework. The central mechanistic insight is that RE^{3+} ions act as 'super-modifiers' of the borosilicate network, generating $BO_3 \rightarrow BO_4$ conversion at a rate approximately three times more efficient per mole than equivalent alkali oxide modifiers. This structural conversion simultaneously stiffens the network (raising T_g), reduces thermal expansion (lowering CTE), and enriches the local environment of embedded RE optical centres (lowering phonon energy, raising σ_{em}). A nuanced but important finding is the non-linearity of the dn/dT response above 1 mol% RE_2O_3 (not fully captured in the present dataset but suggested by the $R^2 = 0.787$ for this correlation). This non-linearity is attributed to the emergence of RE-rich nanoscale heterogeneities — proto-clusters — that alter the local dielectric response faster than the macroscopic compositional change would predict. Future TEM and small-angle X-ray scattering (SAXS) characterisation of 2 and 3 mol% compositions will be essential to map this

transition quantitatively. The comparison across RE dopants reveals a clear design hierarchy for different applications. For maximum thermal stability with photonics activity: Yb³⁺ at 1.0 mol% (highest T_g, lowest CTE, highest N₄). For maximum amplifier gain at 1.53 μm: Er³⁺ at 1.0 mol% (highest σ_{em}, longest τ_{rad}, highest χ⁽³⁾). For high-power solid-state lasers at 1.06 μm: Nd³⁺ at 0.5–1.0 mol% (highest σ_{em} at 1.06 μm, acceptable T_g). For radiation-hard shielding glass with optical function: Gd³⁺ at 0.5 mol% (moderate thermal improvement, large neutron capture cross-section). A significant implication of the ΔT correlation (r = 0.994 with T_g) is that simple DSC measurement of T_g alone provides a reliable proxy for the full thermal processing window. This practical guideline substantially reduces characterisation burden in industrial glass development workflows.

7. Conclusion

This study has demonstrated, through a comprehensive experimental dataset on nine borosilicate glass compositions, that rare earth ion identity (encoded principally by ionic field strength, Z/r²) and concentration are the dominant compositional variables governing both thermal stability and thermo-optical performance. The key conclusions are: The conversion of boron coordination from trigonal (BO₃) to tetrahedral (BO₄) is the primary structural mechanism linking RE ion identity to all thermal and optical property changes, and is directly quantifiable by FTIR deconvolution of the N₄ fraction. Glass transition temperature T_g correlates with ionic field strength with r = 0.962 (p < 0.001), rising from 563 °C (undoped) to 591 °C (1 mol% Yb³⁺). The thermal stability window ΔT correspondingly increases by 7.7%. The CTE decreases systematically with RE field strength (from 3.21 to 3.08 × 10⁻⁶ K⁻¹), exploiting the network rigidification from BO₄ enrichment. This provides a tunable thermal expansion coefficient around the excellent baseline value of borosilicate glass. Refractive index correlates near-linearly with RE concentration (r = 0.978), driven by the increasing molar polarizability of 4f electron shells. The thermo-optical coefficient dn/dT becomes monotonically more negative (-4.2 to -5.8 × 10⁻⁶ K⁻¹), enabling precisely tunable athermal optical design. Judd–Ofelt analysis confirms that the BO₄-enriched host environment — achieved by high-field-strength RE doping — reduces phonon energy and enhances stimulated emission cross-sections. BSG-Er1.0 achieves σ_{em} = 7.14 × 10⁻²¹ cm² at 1.53 μm, competitive with commercial EDFA gain media. A Unified Structure–Thermal–Optical Correlation Framework, supported by six statistically significant bivariate correlations (r ≥ 0.887), is established, enabling predictive composition design for RE-doped borosilicate photonic glasses without exhaustive trial-and-error synthesis.

Future work should extend this framework to concentration series beyond 1.0 mol%, investigate co-doped systems (Er³⁺/Yb³⁺ for EDFA sensitisation), apply SAXS/TEM for nanoscale cluster characterisation, and model the dn/dT–temperature relationship using finite-element thermo-optical simulation for device-level design validation.

References

1. Scientific Reports (2026). Influence of six different RE³⁺ ions as modifier agents on the photoluminescent, electrical, magnetic and thermal properties of B-Na glass. Nature Portfolio.
2. Scientific Reports (2024). Comparative study on the influence of rare earth ion doping on the structural and optical properties of simple B₂O₃–Na₂O glasses. Nature Portfolio.
3. Scientific Reports (2024). Newly developed CeO₂ and Gd₂O₃-reinforced borosilicate glasses from municipal waste ash and their optical, structural, and gamma-ray shielding properties.
4. Scientific Reports (2024). Enhanced optical and structural traits of irradiated lead borate glasses via Ce³⁺ and Dy³⁺ ions with studying radiation shielding performance.
5. Trends in Sciences (2024). A Review of Rare Earth Ion-Doped Glasses: Physical, Optical, and Photoluminescence Properties. Trends Sci. 21(12): 8759.

6. MDPI Materials (2021). Effect of Rare-Earth Ions on the Optical and PL Properties of Novel Borosilicate Glass Developed from Agricultural Waste. *Materials*, 14, 5607.
7. MDPI Nanomaterials (2024). Investigating the Mechanism of Rare-Earth Ion Incorporation into Glass–Ceramic Crystal Phases through Er^{3+} Ion Probe Characteristics. *Nanomaterials*, 14(18), 1479.
8. *Frontiers in Physics* (2024). Research status of rare-earth-ion-doped infrared laser. *Front. Phys.* 12.
9. ScienceDirect / *Journal of Luminescence* (2021). Spectroscopic investigations on 1.53 μm NIR emission of Er^{3+} doped multicomponent borosilicate glasses for telecommunication and lasing applications. *J. Lumin.* 233, 117912.
10. ScienceDirect / *Optics and Laser Technology* (2024). Er^{3+} doped low-melting lead borosilicate glass for laser applications. *J. Lumin.* 266, 120249.
11. ScienceDirect / *Spectrochimica Acta A* (2023). Spectral characterization and energy transfer study of $\text{Nd}^{3+}/\text{Yb}^{3+}$ in borosilicate glasses. *Spectrochim. Acta A*, 295, 122589.
12. ScienceDirect / *Journal of Luminescence* (2022). Temperature dependence of spectroscopic properties and energy transfer in $\text{Nd}^{3+}/\text{Yb}^{3+}$ co-doped silicate glass. *J. Lumin.* 247, 118926.
13. *Ceramics International* (2024). Evaluating the role of Er^{3+} ion on the structural, optical and thermal properties of $\text{CaO-ZrO}_2\text{-Y}_2\text{O}_3\text{-B}_2\text{O}_3\text{-SiO}_2$ glasses. *Ceram. Int.* 50, 39898–39906.
14. Wikipedia / RP Photonics (2024). Borosilicate glass. Physical and optical properties. https://en.wikipedia.org/wiki/Borosilicate_glass; RP Photonics Encyclopedia: Optical Glasses.
15. Judd, B. R. (1962). Optical absorption intensities of rare-earth ions. *Physical Review*, 127(3), 750–761.
16. Ofelt, G. S. (1962). Intensities of crystal spectra of rare-earth ions. *The Journal of Chemical Physics*, 37(3), 511–520.
17. McCumber, D. E. (1964). Theory of phonon-terminated optical masers. *Physical Review*, 134(2A), A299.
18. Shannon, R. D. (1976). Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. *Acta Crystallographica A*, 32, 751–767.
19. Kaur, R., Singh, A. K., Singh, V., & Singh, M. (2019). Physical, structural, optical and thermoluminescence behavior of Dy_2O_3 -doped sodium magnesium borosilicate glasses. *Results in Physics*, 12, 827–839.