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Optical Characteristics of Chromium Oxide Doped Bismuth Borate Glasses

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ABSTRACT

The glasses, composed of multiple components, contain chromium oxide $x.Cr_2O_3.(70\text{-}x)B_2O_3.18Bi_2O_3.12Na_2O$, where x varies (x=0, x=0.15, x=0.25, x=0.35, x=0.50 mol %), synthesized using the melt-quench method. The amorphous nature of the synthesized samples was confirmed using X-ray diffraction (XRD). We observed that an increase in Cr_2O_3 content resulted in a rise in the density (ρ) of the glasses, ranging from 3.88 g/cm^3 to 4.009 g/cm^3. The molar volume displays behavior opposite to the density and oxygen packing density (OPD) trends exhibited augmentation with elevated chromium oxide concentration. Optical absorption spectra have been recorded within the frequency range of 200 to 3200 nm. The UV-VIS absorption spectra of polished glass samples with parallel surfaces revealed a reduction in the optical band gap (E_g) as the Chromium content increased. These findings provide a foundational basis for customizing glass compositions to meet specific technological requirements, encompassing applications in optics and radiation shielding. Recorded spectra are analysed to evaluate refractive index (n), optical band gap (E_g) and Tauc's plots, Urbach energy (E_u).

Keywords: XRD, Density, Molar volume, UV-Vis, Refractive index, Urbach

INTRODUCTION

Glasses attract significant interest owing to their diverse array of properties and applications, spanning non-linear optics, solar conductors, solid-state lasers, actuators, optoelectronic devices, and radiation shielding. The bismuth borate system as a host is driven by its exceptional features, including a high refractive index, high density, broad transmission ranges from UV to IR, and a high dielectric constant [1-2]. This characteristic renders them well-suited for applications in the domain of non-linear optics, ultrafast optical switches, and photonic devices. Despite these advantages, ongoing efforts are focused on improving the optical, electrical, mechanical, and thermal characteristics of bismuth-borate glasses [2-3].

Over the last four decades, borate glass has emerged as a material of significant interest due to its promising mechanical and optical properties. These attributes have spurred exploration for potential applications in both industrial and medical fields. Research indicates that the presence of small quantities of alkali and alkaline elements as modifiers, along with lanthanides as dopants, enhances the properties of borate glasses [3-5]. Chromium oxide, a transition metal ion, has significant interest due to its unique absorption and emission properties. Even in small concentrations within glass, it imparts color and influences optical and dielectric properties. The Cr^{3+} ion is valuable for investigating structural intricacies within glassy materials and serves as a probe in nonmaterial studies. Additionally, chromium oxide is commonly used in polishing materials like leather and optical devices [6-7], Borate glass is highly regarded for its mechanical and optical properties, drawing attention in recent years. Incorporating chromium oxide (Cr_2O_3) can tailor the glass for applications in lasers and high-temperature environments. This study explores the addition of Na_2O and Chromium to bismuth borate glasses, examining their transformation into crystalline structures and investigating physical, mechanical, and optical properties using UV analysis [7-11]. The research aims to comprehensively understand the structural implications of chromium ions in multi component bismuth borate glasses, synthesizing glasses with varying amounts of Cr_2O_3 and analyzing their properties. Consequently, glasses with the compositional formula $x.Cr_2O_3.(70\text{-}x)B_2O_3.18Bi_2O_3.12Na_2O$ are synthesized with varying amounts of chromium oxide. The synthesis procedure and physical properties have been thoroughly investigated and reported, with a focus on examining their variations.

EXPERIMENTAL PROCEDURE

Multi-component bismuth borate glasses underwent modification by adding varying amounts of chromium oxide, according to the formula $x.Cr_2O_3$. $(70\text{-}x)B_2O_3.18Bi_2O_3.12Na_2O$, where x ranges from 0 to 0.50 Wt%. These compositions were labeled CRBBN1 to CRBBN5. In the synthesis, chromium oxide and sodium oxide were substituted for boron oxide, following specific weight percentages outlined in Table 1. The synthesis procedure included grinding and transferring the chemicals into crucibles, which were then heated in an electric furnace at 1200K for 45 minutes [4-7]. Samples were extracted from the furnace at the end of this period and promptly moved into a preheated furnace at 400°C to remove the thermal stress. Subsequently, the furnace was permitted to cool down to room temperature. Following this, the samples were sectioned, polished, and resized appropriately for measurement purposes [5-10].

Table. 1: Chemical composition of CRBBN glass batch in mol%

		The ratio of each component's mol %			
Glass labelled	**Composition X values**	**Cr_2O_3**	**B_2O_3**	**Bi_2O_3**	**Na_2CO_3**
CRBBN1	0	0	70	18	12
CRBBN2	0.15	0.15	69.85	18	12
CRBBN3	0.25	0.25	69.75	18	12
CRBBN4	0.35	0.35	69.65	18	12
CRBBN5	0.50	0.50	69.50	18	12

EXPERIMENTAL RESULTS AND INTERPRETATIONS

XRD Analysis of Glass Composition

To obtain information about the structural characteristics of the prepared samples, we conducted powder X-ray diffraction (XRD) analysis in the range of 10° to 80°, as illustrated in **Figure 1**. This analysis offers insights into whether the samples possess a crystalline or amorphous nature. All prepared samples exhibit broad peaks at around 25° and 45degree. These broad peaks in the XRD patterns are indicative of short-range order, further confirming the amorphous or glassy nature of the prepared samples [5-9]. The optical absorption spectra of the synthesized CRBBN glasses were analyzed by a UV770 V-770 spectrophotometer. Well-polished samples were employed to record UV-Vis absorption spectra across the range of 400nm to 900nm [10-11].

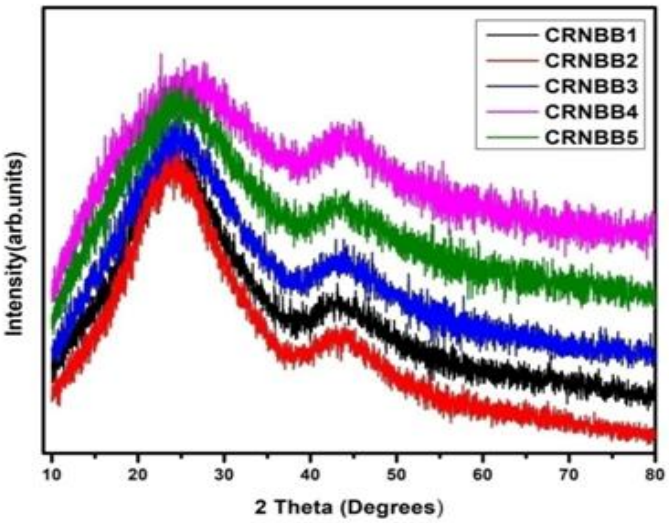

Fig. 1 XRD patterns of quenched samples with different contents of Chromium oxide

Optical absorption spectra of studied glass system

UV-Vis. spectroscopy

The optical spectra, spanning wavelengths from 200 to 2000 nm, reveal the electromagnetic radiation interactions with the material. In this range, the absence of sharp absorption edges, as depicted in **Figures 2 and 3**, indicates the glassy nature of the material. Optical absorption coefficients (α) serve as a widely used approach for investigating electronically induced transitions in materials under optical excitation [5].

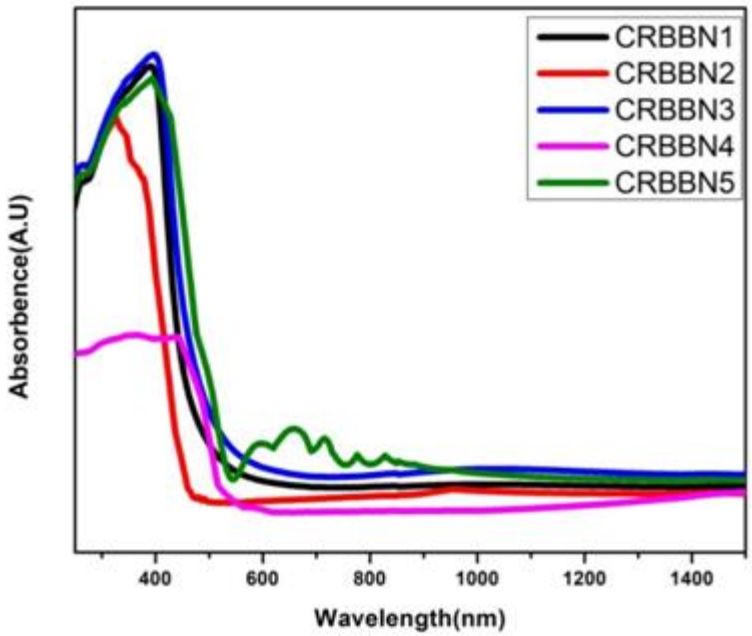

Fig. 2 Absorbance spectrum of composition $x.Cr_2O_3.(70\text{-}x)B_2O_3.18Bi_2O_3.12Na_2O$, where x varies (0, 0.15, 0.25, 0.35, 0.50 mol %).

At the absorption coefficients at the edge, direct and in-direct optical transitions were determined by using different wavelengths. The absorption coefficients at the edges of the plotted curve were deceived by considering the wavelengths from the relation [9-11]:

$$\alpha(\nu) = \left(\frac{1}{t}\right) \ln\left(\frac{Io}{I_t}\right) \quad (1)$$

From the transmittance graph, it has been noted that the prepared glasses show zero transmission around 400nm and a sharp rise in transmission beyond the cut-off wavelength in the IR region [14-16].

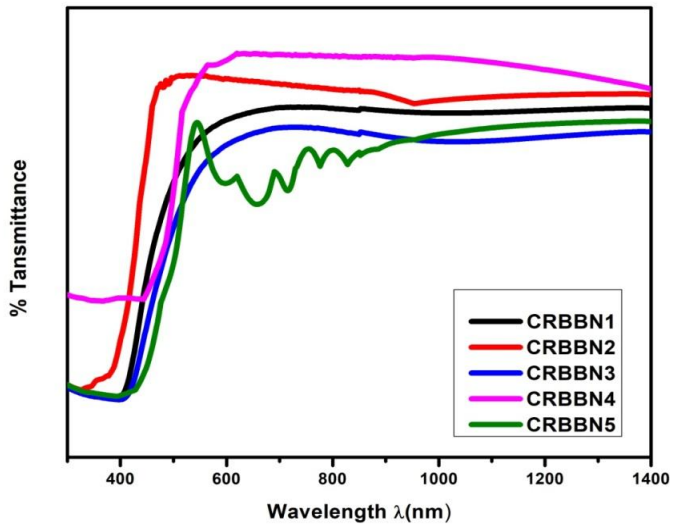

Fig. 3 Transmittance spectrum at room temperature of composition $x.Cr_2O_3.(70\text{-}x)B_2O_3.18Bi_2O_3.12Na_2O$, for varying concentration.

The CRBBN glasses exhibit a characteristic green colour, with all glass samples in the system displaying a prominent central peak around 550nm. This can be attributed to the presence of chromium oxide, which boasts a broad optical window

spanning from UV to IR wavelengths**.** Samples thickness represented by "t," the ratio of transmitted light intensity (I_t) to incident light intensity (I_o) provides insight into the absorbance coefficient α(ν), calculated as $\ln(I_0/I_t)$. According to Davis and Mott's Tauc's theory, there exists a constant 'B' linking incident photon energy (hν) with an index parameter 'r', which can take values such as 2, 3, 1/2, and 1/3. These values correspond to various types of transitions, including direct forbidden, direct allowed, indirect forbidden and indirect allowed transitions. Tauc's theory, primarily applicable to amorphous materials, underscores the importance of indirect allowed and forbidden transitions in determining their optical properties.

$$\boldsymbol{\alpha(h\nu) = B\left(h\nu - E_{opt}\right)^{r}} \quad (2)$$

This relation is used for plots showing the graphical representations in **Figure 4, 5** indirect transitions $(\alpha h\nu)^{1/2}$, $(\alpha h\nu)^{1/3,}$ and photon energy (hν).The values obtained from this exhibit a systematic reduction in optical bandgap energies for both indirect allowed and forbidden transitions. The increase in NBOs creates states inside the energy gaps, which in turn reduces the band gap energy [12]. Urbach's energy (E_u) is a parameter calculated for the current glass sample by taking the reciprocal of the straight line. The relationship between the natural logarithm of the absorption coefficient and incident photon energy α(ν) is established by Urbach's energy. **Figure 7**, **Table 2** lists the calculated E_u values [12-13]. It provides information and the presence of defects in the material.The theoretical Urbach rule provides the relationship between E_u and α (ν).

Table 2. Various Optical Characteristics Band gap energy, and Urbach energy as shown below.

Sample	Eg(eV) r=2	Eg(eV) r=3	slope (ΔE)	Urbach energy(E_U)
CRBBN 1	2.59	2.42	2.368	0.42
CRBBN 2	2.44	2.29	2.519	0.40
CRBBN 3	2.42	2.21	2.674	0.37
CRBBN 4	2.33	2.13	2.784	0.36
CRBBN 5	2.24	2.01	2.930	0.34

$$\boldsymbol{\alpha(\nu) = \beta exp\left(\frac{h\nu}{E_u}\right)} \quad (3)$$

According to Mott-Davis, Urbach energy values for amorphous semiconductors typically range from 0.045 to 0.66. A decrease in Urbach's energy value indicates enhanced structural stability, reduced defect concentration, and less electron delocalization.

Table. 3 Various optical parameters of glass system with the composition, Dielectric constant (ε), Metallization criterion(M), Molar polarizability (α_m), Molar reflectivity R_m (cm^3 /mol), Reflection loss (R_L), Refractive index(n), Transmission coefficient(T)of chromium oxide as listed in the table:

Parameters	CRBBN 1	CRBBN 2	CRBBN 3	CRBBN 4	CRBBN 5
Refractive index(n)	2.517	2.566	2.573	2.605	2.638
Dielectric constant(ε)	6.335	6.584	6.62	6.786	6.959
Electronegativity (χ)	0.696	0.655	0.650	0.626	0.602
Electron polarizability(α^-)	2.873	2.909	2.914	2.936	2.958
Optical dielectric constant (ε_{opt})	5.335	5.58	5.62	5.786	5.959
Optical Basicity (∧)	1.351	1.372	1.374	1.386	1.398
Metallization criterion(M)	0.359	0.349	0.348	0.341	0.334
Molar polarizability(αm)	9.304	9.346	9.29	9.296	9.247
Molar reflectivity R_m (cm^3 /mol)	23.44	23.55	23.425	23.426	23.30
Reflection loss (R_L)	0.640	0.650	0.651	0.658	0.665
Transmission coefficient(T)	0.686	0.676	0.675	0.669	0.662

The molar refractivity (R_m) by the given relation

$$\boldsymbol{R_m = V_M\left[1 - \sqrt{\frac{Eg}{20}}\right]} \quad (4)$$

The Lorentz-Lorenz equation establishes a direct relationship between a material's molar refractivity and molar polarizability. It shows how much electrons react when an electric field is introduced.

$$\boldsymbol{\alpha_m = \left(\frac{3}{4\Pi N}\right) R_m \ = \frac{R_m}{2.52}} \quad (5)$$

Reflection loss can be calculated using the relation of R_M and V_M

$$\mathbf{R_L} = \frac{\mathbf{R_m}}{\mathbf{v_M}} \quad \textbf{(6)}$$

$$\mathbf{M} = \mathbf{1} - \frac{\mathbf{R_m}}{\mathbf{v_M}} \quad (7)$$

there are specific conditions that indicate the non-metallic nature of solids. In this framework, if the reflection loss value approaches one, it indicates a metallic character of the material, ($\frac{\mathbf{R_m}}{\mathbf{v_M}} > 1$) Conversely, when the reflection loss value deviates from one, it suggests a non-metallic nature of the material, $\frac{\mathbf{R_m}}{\mathbf{v_M}} < 1$ .Therefore, in the present dataset, the metallization criterionranged from (0.35 to 0.33) that balances metallic and insulating characteristics can be applied to ascertain whether the material is metallic or non-metallic based on the relationship between the molar refractivity (R_M) and molar volume (V_M).

The Transmission coefficient is,

$$\mathbf{T} = \frac{\mathbf{2n}}{\mathbf{n^2+1}} \quad (8)$$

The refractive index [14] of glass is according to using optical band gaps

$$\frac{\mathbf{n^2-1}}{\mathbf{n^2+2}} = \left[\mathbf{1} - \sqrt{\frac{\mathbf{Eg}}{\mathbf{20}}}\right] \quad (9)$$

The refractive index of glass serves as a valuable parameter for investigating glass materials that can be employed in optical devices. The refractive index experiences a rise from 2.51 to 2.64 as the chromium content increases. This observed pattern is per earlier research on chromium-doped glasses, where in higher concentrations of chromium induce an upsurge in the refractive index .The dielectric constant and optical dielectric constant values are determined using the following equations:

$$\boldsymbol{\varepsilon} = \boldsymbol{n^2} \quad (10)$$

$$\boldsymbol{\varepsilon_{opt}} = \boldsymbol{\varepsilon} - 1 \quad (11)$$

The electronegativity of an ion can be described as a measure of how strongly it attracts electrons from bonded oxide ions. It can be calculated by

$$\boldsymbol{\chi} = \mathbf{0.2688Eg} \quad (12)$$

Using the electronegativity relation two more factors are determined electron polarizablity and optical basicity.

$$\boldsymbol{\alpha_0} = \mathbf{-0.9\chi + 3 \cdot 5} \quad (13)$$

$$\boldsymbol{\Lambda} = \mathbf{-0.5\chi + 1 \cdot 7} \quad (14)$$

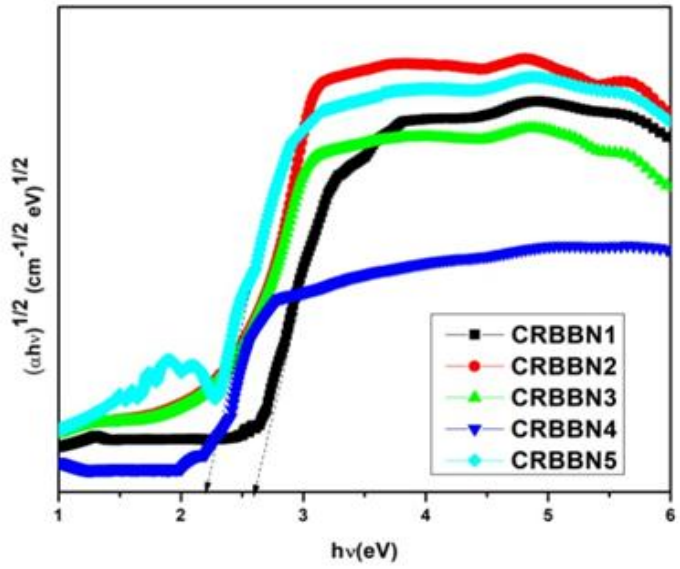

Fig. 4 Tauc's plots for composition x.Cr_2O_3.(70-x)B_2O_3.18Bi_2O_3.12Na_2O, for varying concentration the values from (0, 0.15, 0.25, 0.35, 0.50 mol %).

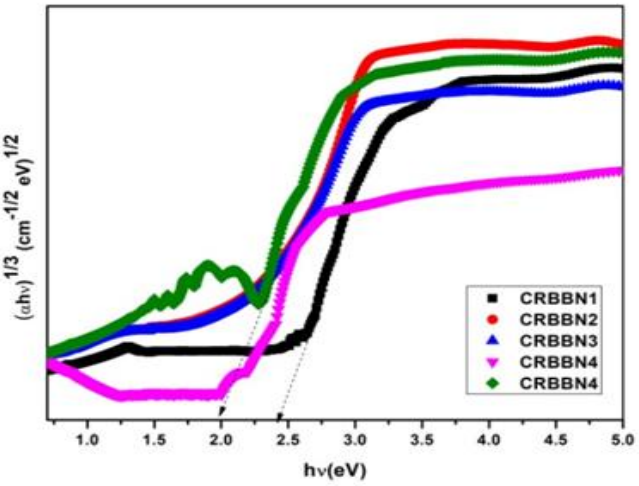

Fig. 5 Tauc's plots for (r=3) composition $x.Cr_2O_3.(70-x)B_2O_3.18Bi_2O_3.12Na_2O$, for varing concentration for x is (0, 0.15, 0.25, 0.35, 0.50 mol %).

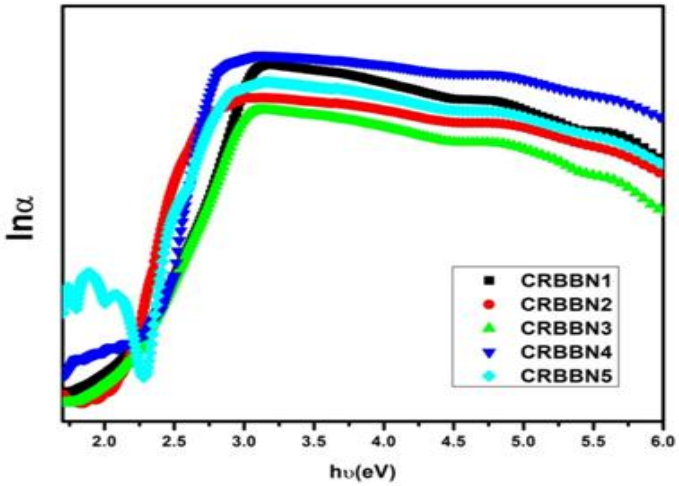

Fig. 6 Urbach energy plots for samples CRBBN1, CRBBN2, CRBBN3, CRBBN4, CRBBN5 of the glass system.

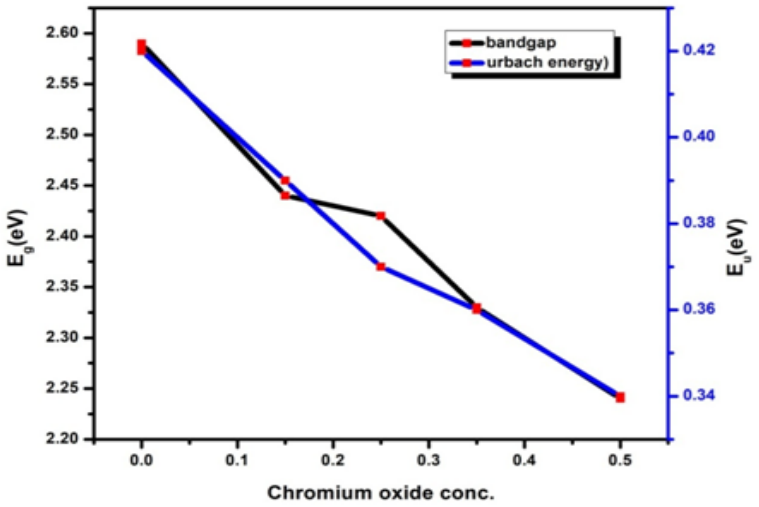

Fig. 7 The correlation between the molar concentration of chromium and both the band gap and Urbach energy

The analysis of refractive index values indicates a nonlinear increase with the progressive addition of chromium to the glass composition [14-17]. This increase in band gap reduces light interaction, particularly with photons of specific frequencies, within the material. As chromium content increases, transmission coefficient and reflection loss show divergent patterns. These findings enhance our understanding of glass's optical behavior and its potential applications across various domains.

CONCLUSION

Glasses incorporating sodium in the bismuth borate system with chromium ions were fabricated using the melt quenching technique. Subsequently, the samples were subjected to X-ray diffraction analysis to ascertain their amorphous nature. The amorphous nature is very well predicted by the XRD measurements, followed by UV-visible absorption studies to investigate optical properties such as refractive index Urbach energy. The absorption edge shifts towards longer wavelengths with increasing concentrations of TM ions. The index of refraction 'n' increases, which tends to increase the concentration of (NBOs) and contribute to E_g bandgap energy decreases. E_g diminishes as the Chromium oxide content progressively increases. The Urbach energy value decreases from 0.42 to 0.34, the decreasing value indicates the increased structure stability and defect concentration, and the delocalization of the electron will decrease this suggests potential applications of the CRBBN glass system in optical devices.

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Author Contributions
Deepika Maan: Writing the initial and final draft of the manuscript reviewing and editing. Material preparation, data collection and analysis. Meenakshi: Supervision.

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Data Availability
Data that supports the research will be made available upon reasonable request. We believe in the importance of open and transparent research practices and are committed to providing access to our data to promote collaboration and further scientific inquiry.

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Declarations
Conflict of Interest: We have no relevant financial or non-financial interests to disclose.
I declare that I have no competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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