

Probing Network Depolymerization and NBO Creation in Na₂O-Sb₂O₃ Glasses via Site-Sensitive Eu³⁺ Photoluminescence

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Abstract— This study investigates (99.8-x) Sb₂O₃-xNa₂O-0.2Eu₂O₃ glass (10Na-40Na) using FTIR and Eu³⁺ site-sensitive photoluminescence. FTIR spectroscopy reveals progressive network depolymerization, with non-bridging oxygen (NBO) bands appearing at 300Na-40Na (~1017 and ~833 cm⁻¹). Deconvolution of the Eu³⁺ ⁵D₀→⁷F₀ emission demonstrates a spectral shift from 576 nm to a nephelauxetically red-shifted 578 nm peak at higher modifier contents. This optical evolution confirms that while Na⁺ continues promoting [SbO₆] unit formation, higher concentrations (300Na-40Na) additionally drive a network-modifying role that generates polarizable NBOs, causing matrix reorganization and altering the local symmetry around Eu³⁺ ions.

Heavy metal oxide glasses based on antimony oxide (Sb₂O₃) have drawn substantial research interest due to their high refractive index, broad optical transmission windows, and low phonon energies. In vitreous networks, antimony displays complex structural behaviour depending on glass composition and synthesis conditions. While pristine antimonate or binary borate antimonate matrixes predominantly incorporate trivalent antimony (Sb³⁺) in the form of [SbO₃E] trigonal pyramids or [SbO₄E] polyhedral (where E represents the 5s² lone pair of electrons), modification with alkali or alkaline earth oxides promotes the oxidation of a fraction of Sb³⁺ into pentavalent Sb⁵⁺[1–4].

Understanding how alkali incorporation dictates the balance and structural transformations among these antimonies polyhedral is vital for tailoring glass network properties. The addition of Na⁺ ions introduces modifier oxygen species and alters local basicity, directly shifting the redox equilibrium and coordination behaviour of the antimony oxide framework. To probe these local structural dynamics at the molecular scale, trivalent europium (Eu³⁺) serves as an exceptionally sensitive local structural probe.

The unique photoluminescence characteristics of Eu³⁺ enable precise characterization of local site symmetry and chemical environment changes in amorphous hosts. Specifically, the extremely narrow, non-degenerate forbidden ⁵D₀→⁷F₀ electronic transition provides direct insight into the number and symmetry of distinct local site

environments. Furthermore, using the magnetic dipole transition (⁷F₀→⁵D₁ at 526 nm) for excitation can stimulate all Eu³⁺ site families regardless of their individual excitation cross-sections. The emitting ⁵D₀ energy level, which becomes populated from ⁵D₁ via non-radiative transitions, is positioned relatively far from the hypersensitive ⁵D₂ energy level. This separation makes the ⁵D₀ state approximately unaffected by J-mixing and keeps its energy position fixed regardless of structural environment changes[5,6].

Therefore, this study aims to reveal the effect of Na⁺ addition on the antimony oxide structural behaviour, composition, and polyhedral coordination (SbO₃, SbO₄, and SbO₆) in binary sodium antimony glasses using FTIR spectroscopy and Eu³⁺ optical site-probing spectroscopy.

Glasses with nominal compositions (99.8-x) Sb₂O₃-xNa₂O-0.2Eu₂O₃ (x = 10, 20 30, and 40 mol%), designated as xNa) were synthesized via the conventional melt-quenching technique in ambient air. Stoichiometric precursor powders (Sb₂O₃, Na₂CO₃, and Eu₂O₃) were thoroughly homogenized in an agate mortar and melted in a corundum crucible. The cast samples were immediately annealed for 4 h at T_g – 20 °C[7], and optically polished. X-ray diffraction (XRD) measurements were conducted on a Bruker D8 Advance diffractometer using Cu K_α radiation. Photoluminescence emission spectra were acquired using a HORIBA Jobin Yvon FluoroMax-4P spectrofluorometer, and FTIR spectra were recorded on a PerkinElmer Spectrum Two spectrometer using attenuated total reflectance (ATR) mode.

The representative X-ray diffraction (XRD) patterns shown in Fig 1 confirm the fully amorphous nature of all glass samples. The complete absence of sharp Bragg reflections indicates the lack of long-range atomic order. Instead, the diffractograms display broad diffuse humps (halos) indicative of short-range structural order.

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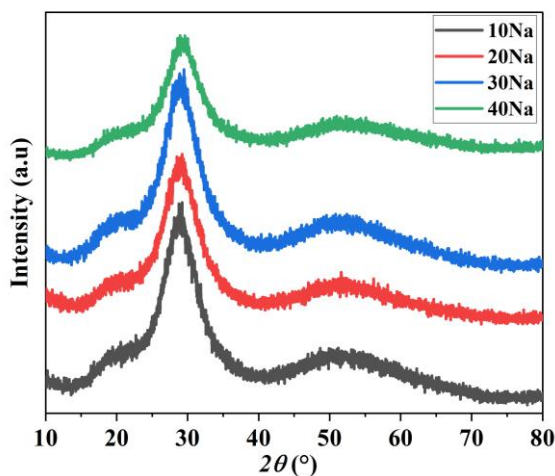


Fig. 1. XRD patterns of xNa glass samples.

The FTIR spectra of the $(99.8-x) \text{Sb}_2\text{O}_3\text{-}x\text{Na}_2\text{O-}0.2\text{Eu}_2\text{O}_3$ glasses (10Na–40Na) show several bands related to Sb–O bending and stretching vibrations. The band at $\sim 405 \text{ cm}^{-1}$ in 20Na shifts to $\sim 434 \text{ cm}^{-1}$ in 30Na and 40Na, indicating modification of Sb–O–Sb deformation environments with increasing Na_2O [1]. The bands at $538\text{--}548$ and $562\text{--}569 \text{ cm}^{-1}$ remain nearly unchanged, suggesting relatively preserved Sb–O bending/deformation environments[8,9]. Similarly, the $663\text{--}676 \text{ cm}^{-1}$ band remains nearly constant up to 30Na but shifts to $\sim 644 \text{ cm}^{-1}$ at 40Na, while the $739\text{--}750 \text{ cm}^{-1}$ band shifts to $\sim 716 \text{ cm}^{-1}$ [8], indicating pronounced rearrangement of the Sb–O network at high Na_2O content. In the higher-wavenumber region, the bands at $860\text{--}887$ and $919\text{--}939 \text{ cm}^{-1}$, attributed to stretching vibrations of Sb(V)-containing SbO_6 environments with pyrochlore-like local configurations, remain approximately unchanged throughout the series[4]. New bands at ~ 1017 and $\sim 833 \text{ cm}^{-1}$ appear from 30Na, which can be associated with non-bridging oxygen (NBO) environments involving Sb(V) and Sb(III), respectively. The earlier appearance of the $\sim 1017 \text{ cm}^{-1}$ band may be related to the charge-compensating role of Na^+ around negatively charged Sb(V)-oxygen units. In contrast, the $\sim 833 \text{ cm}^{-1}$ band becomes evident with the higher Na_2O content and is associated with increasing NBO formation around Sb(III). Overall, the spectral evolution indicates that Na_2O addition progressively depolymerizes and rearranges the Sb–O network and promotes the development of mixed Sb(III)/Sb(V) structural environments. These changes are evident in Fig 2a, while the deconvoluted spectra of 20Na, 30Na, and 40Na are presented in Fig 2b–d, respectively.

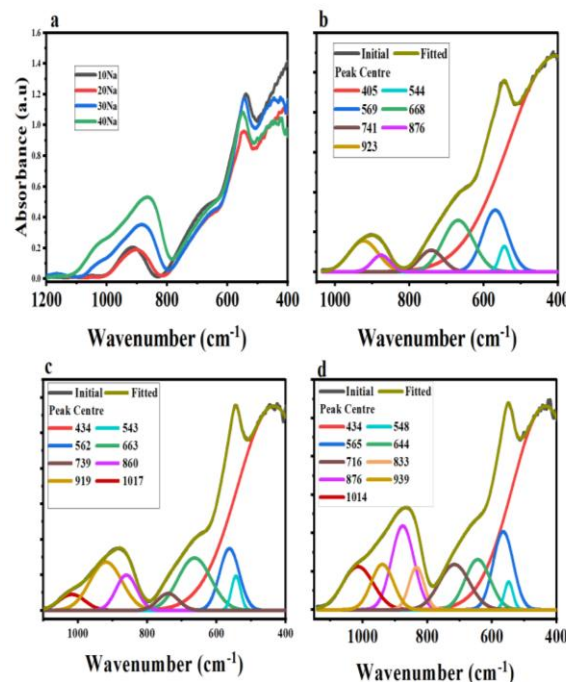


Fig. 2. (a) FTIR spectra of xNa glass samples; peak deconvolutions of (b) 20Na, (c) 30Na, (d) 40Na.

To probe the local structural evolution of the glass matrix, the site-sensitive $^5\text{D}_0 \rightarrow ^7\text{F}_0$ transition of Eu^{3+} was analysed through spectral deconvolution (Fig 3). The emission profiles reveal two distinct Eu^{3+} site families whose relative dominance shifts with Na^+ concentration. In low- Na^+ samples (10Na and 20Na), the spectra are dominated by a high-energy peak centred at 576 nm (Fig 3b, c). Conversely, an inverted spectral behaviour is observed at higher Na^+ concentrations (30Na and 40Na), where the low-energy peak at 578 nm becomes predominant (Fig 3d, e).

This transition directly reflects the dual structural role of Na^+ ions in the host matrix. At low concentrations (10–20Na), Na^+ acts primarily as a charge compensator, assisting in the conversion of trigonal $[\text{SbO}_3]$ units into octahedral $[\text{SbO}_6]^-$ units, with Eu^{3+} ions occupying low-symmetry, charge-compensated environments. However, at higher modifier contents (30–40Na), Charge-neutrality requirements force Na^+ to transition into a network-modifying role, generating non-bridging oxygens (NBOs). The coordination of Eu^{3+} to these highly polarizable NBOs increases metal–ligand bond covalency, which induces a pronounced nephelauxetic red-shift of the $^5\text{D}_0 \rightarrow ^7\text{F}_0$ emission toward lower energy (578 nm)[5,6].



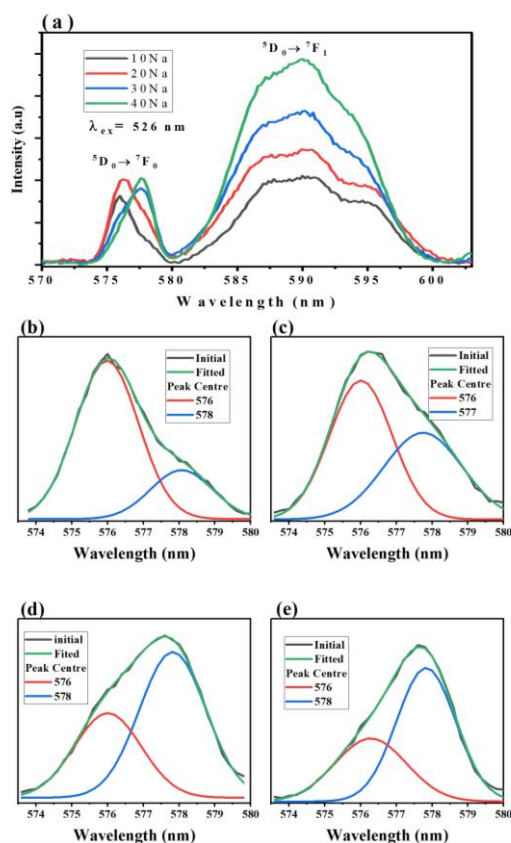


Fig. 3. (a) Emission spectra of xNa glasses excited at 526 nm, and deconvoluted $^5D_0 \rightarrow ^7F_0$ transition peak for (b) 10Na, (c) 20Na, (d) 30Na, (e) 40Na.

Ultimately, the optical response of the Eu^{3+} structural probe offers clear evidence of the glass network's reorganization. The systematic redistribution of Eu^{3+} site families tracks the functional evolution of Na^+ , confirming its shift from a charge-compensating species that supports $[\text{SbO}_6]^-$ formation at low contents to a network modifier responsible for matrix depolymerization through NBO creation at higher concentrations.

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