ISSN No:-2456-2165 https://doi.org/10.38124/ijisrt/26aug1621

# Effect of ZnO on Electrical Conductivity and Activation Energy of Sodium Phosphate Glasses: Evidence Consistent with a Mixed-Modifier Effect

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Publication Date: 2026/09/09

**Abstract: Developing high-performance solid electrolytes for sodium-ion battery architectures requires a fundamental understanding of how network modifiers regulate alkali-ion migration pathways. Here, we examine the structural and electrical properties of a series of sodium zinc phosphate glasses modified with systematically varied ZnO content (x = 0 to 5 mol%). Unlike multi-valent transition metal oxide glass systems, the glasses investigated here behave as purely ionic conductors. Complex impedance plane analyses, conducted over a broad temperature and frequency range, show that the introduction of ZnO alters the structural topology of the sodium phosphate matrix, giving rise to non-linear, composition-dependent changes in DC conductivity and activation energy. X-ray diffraction analysis confirms the fully amorphous, vitreous nature of the synthesized compositions, characterized by broad, diffuse scattering halos. Temperature-dependent electrical resistance was measured using an LCR-Q meter, and conductivity values were calculated from the measured resistance and sample geometry. The temperature dependence was analyzed using an Arrhenius relation. At 200 °C, the reported conductivity decreased from $5.434 \times 10^{-6}$ $\Omega^{-1}$ $cm^{-1}$ for x = 0 to $0.088 \times 10^{-6}$ $\Omega^{-1}$ $cm^{-1}$ for x = 1 mol% ZnO, then increased to $1.244 \times 10^{-6}$ $\Omega^{-1}$ $cm^{-1}$ at x = 4 mol% before decreasing at x = 5 mol%. The activation energy varied between 0.729 and 0.948 eV and broadly followed the inverse conductivity trend. The non-monotonic composition dependence is consistent with a mixed-modifier effect associated with the coexistence of $Na^+$ and $Zn^{2+}$ environments in the phosphate network. Because the measurements were obtained at a single operating frequency rather than by broadband impedance spectroscopy, the measured quantity is conservatively described as electrical conductivity at the measurement frequency rather than rigorously separated dc ionic conductivity.**

***Keywords:*** *Sodium Phosphate Glass; ZnO; Electrical Conductivity; Activation Energy; Mixed-Modifier Effect; Arrhenius Relation.*

**How to Cite:** Sagar Vijay Kale (2026) Effect of ZnO on Electrical Conductivity and Activation Energy of Sodium Phosphate Glasses: Evidence Consistent with a Mixed-Modifier Effect. *International Journal of Innovative Science and Research Technology*, 11(8), 3218-3223. https://doi.org/10.38124/ijisrt/26aug1621

## I. INTRODUCTION

Phosphate-based glasses have emerged as a highly versatile class of glassy materials, attracting significant research interest for solid-state electrochemical applications, including solid electrolytes and bioactive substrates. Unlike conventional silicate networks, the structural framework of vitreous phosphorus pentoxide ($P_2O_5$) is composed of corner-sharing ($PO_4$) tetrahedra, which can tolerate exceptionally high concentrations of alkali oxides while retaining their glassy, disordered character [1]. This compositional flexibility is particularly advantageous for solid-state sodium-ion transport, as it permits the incorporation of substantial quantities of mobile sodium $Na^+$ ions to optimize ionic conductivity [ 9,11]. However, the practical application of simple binary sodium phosphate glasses has historically been bottlenecked by their high hygroscopicity, poor chemical durability, and low thermal stability [1, 12].

To overcome these structural limitations, the introduction of divalent modifier cations has become a primary strategy for modifying the phosphate framework [5, 6]. When a divalent metal oxide, such as zinc oxide ZnO, is incorporated into an alkali phosphate glass matrix, it induces a profound reorganization of the network topology [7]. Zinc ions $Zn^{2+}$ are known to exhibit a dual structural role depending on the local composition [7]. They can coordinate with non-bridging oxygen (NBO) atoms of adjacent phosphate chains, acting as network cross-linkers that bridge neighboring $PO_4$ tetrahedra [1,7]. This cross-linking process

ISSN No:-2456-2165 https://doi.org/10.38124/ijisrt/26aug1621

typically enhances the mechanical rigidity and chemical durability of the glass while raising the glass transition temperature ($T_g$) [1, 5, 6]. Concurrently, this consolidation of the glass matrix significantly alters the structural pathways, free volume, and electrostatic potential landscape experienced by the mobile $Na^+$ charge carriers [5, 6,7].

The physical properties and ion-transport kinetics of these glasses do not scale linearly with compositional variations [5,6]. Instead, they frequently exhibit pronounced non-linearities, a phenomenon commonly referred to as the mixed-modifier effect (MME) or mixed-glass-former-like effect [5, 6]. This non-monotonic composition dependence is characterized by localized minima or maxima in both thermodynamic properties and electrical parameters—most notably the direct-current (DC) ionic conductivity $\sigma_{DC}$ and its corresponding activation energy $E_a$ [5,6]. While the classical mixed-alkali effect in glasses is traditionally attributed to the unequal vibrational dynamics of dissimilar mobile ions [4, 7], the mixed-modifier effect in systems containing both monovalent $Na^+$ and divalent $Zn^{2+}$ modifiers arises from a complex interplay between coordinate compaction, spatial pathway blocking, and network restructuring [5,6]. Understanding how divalent zinc ions partition within the phosphate network is therefore essential to tailoring the ionic mobility of these materials [7].

Importantly, unlike transition-metal-doped glass networks where charge transport is dominated by mixed ionic-polaronic conduction (governed by electron hopping between variable-valence states like $V^{4+}/V^{5+}$ [10, 11], the glass series under investigation in this study behaves as a purely ionic conductor. Charge transport in these materials is dictated exclusively by the long-range hopping of $Na^+$ ions through a structurally rigid oxide framework [16]. This makes the sodium zinc phosphate glass system an excellent model for exploring the fundamental physics of pure ionic transport and structural relaxation in disordered solids [3, 8].

In the present work, ternary glasses with nominal composition $42.5Na_2O:(57.5-x)P_2O_5:xZnO$, where x = 0, 0.5, 1, 2, 3, 4 and 5 mol%, were prepared by melt quenching. XRD was used to assess the amorphous character, while temperature-dependent resistance measurements were used to determine conductivity and Arrhenius activation energies. The observed non-monotonic dependence on ZnO content is examined in the context of a possible mixed-modifier effect between $Na^+$ and $Zn^{2+}$.

## II. EXPERIMENTAL

➢ *Glass Preparation*

High-purity (99.9%) sodium carbonate ($Na_2CO_3$), phosphorus pentoxide ($P_2O_5$) and zinc oxide (ZnO) were used as starting materials. Ternary glasses with nominal composition $42.5Na_2O:(57.5-x)P_2O_5:xZnO$, where x = 0, 0.5, 1, 2, 3, 4 and 5 mol%, were prepared by the conventional melt-quenching technique [16].

Batch quantities of 10–15 g were accurately weighed in the required molar proportions using a monoplane balance. The components were thoroughly homogenized and melted in a high-quality porcelain crucible in an electrically heated furnace at a controlled heating rate. The furnace temperature was maintained approximately 20 K above the corresponding melting temperature for 30 min. The homogenized melt was rapidly quenched between two aluminium blocks to obtain transparent, bubble-free glass discs approximately 2 cm in diameter and 0.1–0.2 cm thick. Precautions were taken to minimize contamination from the crucible and quenching blocks.

➢ *X-ray Diffraction*

The amorphous nature of the as-quenched glasses was examined using a Seifert XRD 3003 T/T diffractometer with Cu Kα radiation (λ = 1.541 Å) and a nickel filter. The instrument was operated at an accelerating voltage of 40 kV and a tube current of 15 mA. Diffraction patterns were recorded in reflection (Bragg–Brentano) geometry over the 2θ range of 20–80° with a step size of 0.02°. Powdered glass samples were spread as a thick layer on a poly (methyl methacrylate) (PMMA) plate.

➢ *Electrical Conductivity Measurement*

The glass samples were polished to obtain regular square specimens, and silver electrodes were applied to two opposing faces to provide electrical contacts. Each specimen was mounted between two silver electrodes in a sample holder and placed inside an electrically heated furnace. Temperature was monitored using a thermocouple. Resistance was measured with an LCR-Q meter during a controlled cooling cycle.

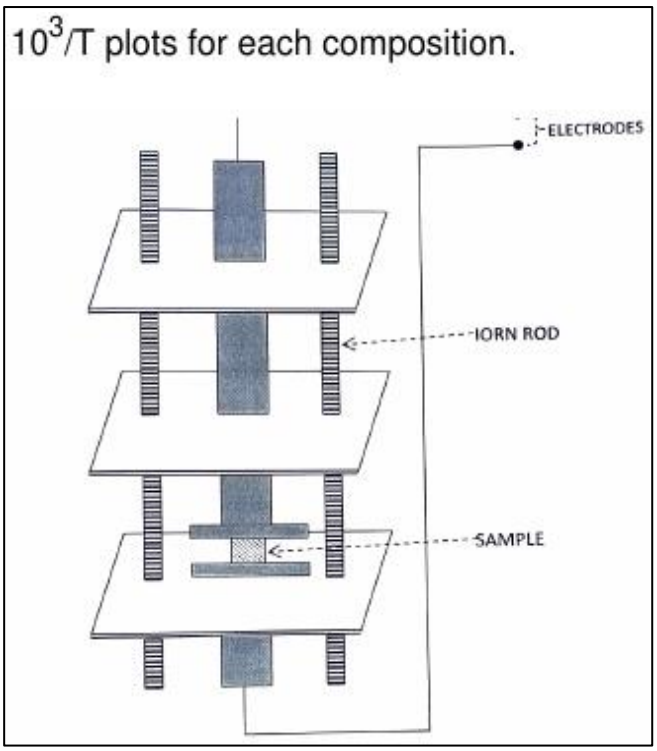


Fig 1 Schematic Representation of the Sample Holder Used for Electrical-Conductivity Measurements

The conductivity at each temperature was calculated using $\sigma = t/(A\,R)$, where t is the specimen thickness, A is the

ISSN No:-2456-2165 https://doi.org/10.38124/ijisrt/26aug1621

electrode contact area and R is the measured resistance. The temperature dependence was analyzed using the Arrhenius relation, $\sigma = \sigma_0 \exp(-E_a/kT)$, where $E_a$ is the activation energy, $\sigma_0$ is the pre-exponential factor and k is the Boltzmann constant. Activation energies were obtained from the temperature dependence of $\log(\sigma T)$ plotted against $10^3/T$ [2,16].

## III. RESULTS AND DISCUSSION

➢ *Structural Characterization*

The XRD pattern of the x = 0.5 mol% ZnO sample displays a broad diffuse halo without distinct sharp Bragg reflections over the measured 2θ range. A similar diffuse profile is observed for the x = 3 mol% ZnO composition. Such broad scattering rather than discrete Bragg reflections is consistent with the absence of long-range crystalline periodicity and is characteristic of an amorphous phosphate-glass network [1,9].

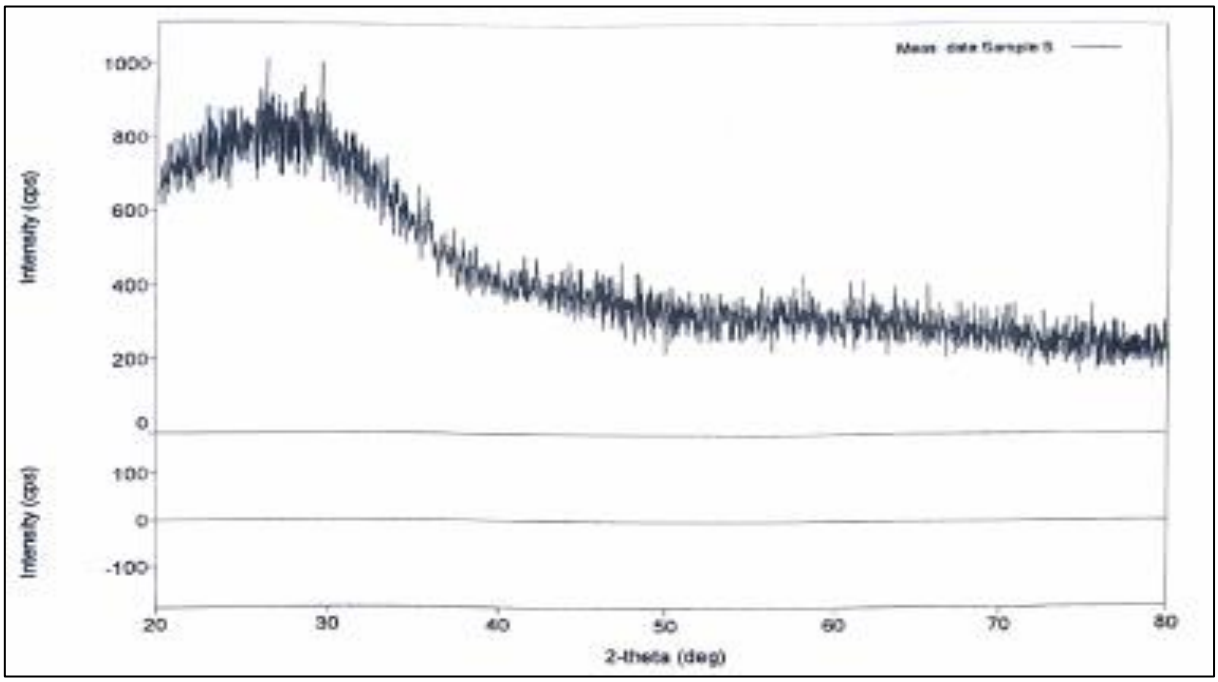


Fig 2 XRD Pattern of $42.5Na_2O:57P_2O_5:0.5ZnO$ Glass

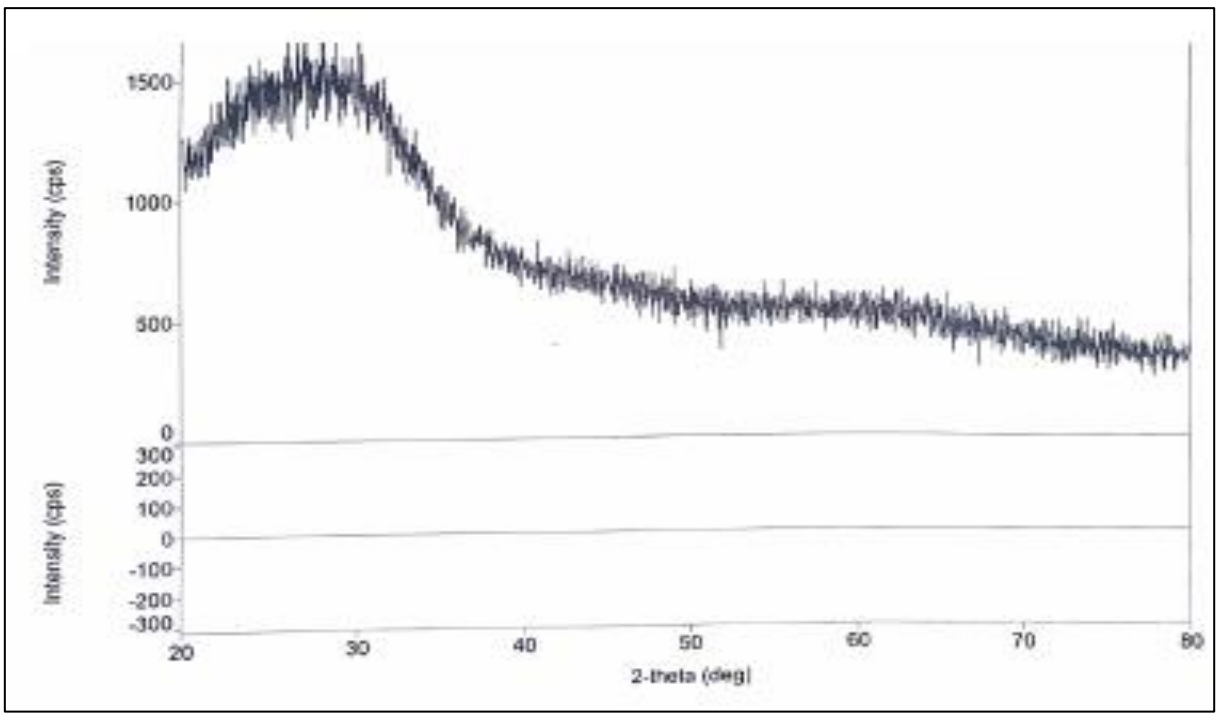


Fig 3 XRD Pattern of $42.5Na_2O:54.5P_2O_5:3ZnO$ Glass

ISSN No:-2456-2165 https://doi.org/10.38124/ijisrt/26aug1621

The submitted manuscript states that all seven compositions exhibited the same amorphous character; however, the presented XRD plots correspond explicitly to x = 0.5 and 3 mol% ZnO. Therefore, the stronger statement that XRD experimentally confirmed all seven compositions should only be retained if diffraction data for the remaining compositions are available. For the present manuscript, the conclusion is restricted to the displayed compositions.

➢ *Electrical Conductivity and Activation Energy*

Table 1 Electrical Conductivity at 200 °C and Arrhenius Activation Energy for the $42.5Na_2O:(57.5-x)P_2O_5:xZnO$ Glass Series.

| ZnO (mol%) | σ at 200 °C ($\Omega^{-1}$ $cm^{-1}$)$10^{-06}$ | log10 σ (200 °C) | $E_a$ (eV) |
|---|---|---|---|
| 0 | 5.434 | -5.2649 | 0.9480 |
| 0.5 | 0.8810 | -6.0550 | 0.7490 |
| 1 | 0.0880 | -7.0555 | 0.7860 |
| 2 | 0.6840 | -6.1649 | 0.7504 |
| 3 | 0.4410 | -6.3556 | 0.8120 |
| 4 | 1.244 | -5.9052 | 0.7289 |
| 5 | 0.966 | -6.0150 | 0.7744 |

The reported log(σT) versus $10^3/T$ plots are approximately linear over the measured temperature range, indicating thermally activated transport that can be represented by an Arrhenius relation within the experimental window [2,16]. At 200 °C, the measured conductivity decreases strongly upon initial ZnO addition, from $5.434 \times 10^{-6}$ $\Omega^{-1}$ $cm^{-1}$ for x = 0 to $0.088 \times 10^{-6}$ $\Omega^{-1}$ $cm^{-1}$ for x = 1 mol%. It then increases to $1.244 \times 10^{-6}$ $\Omega^{-1}$ $cm^{-1}$ at x = 4 mol%, followed by a decrease to $0.966 \times 10^{-6}$ $\Omega^{-1}$ $cm^{-1}$ at x = 5 mol%.

The activation energy changes between 0.7289 and 0.948 eV. The highest value is obtained for the undoped glass, whereas the lowest value occurs at x = 4 mol% ZnO. The inverse tendency between conductivity and activation energy is qualitatively consistent with thermally activated transport, although the magnitude of the composition dependence should be interpreted together with the limitations of the single-frequency measurement.

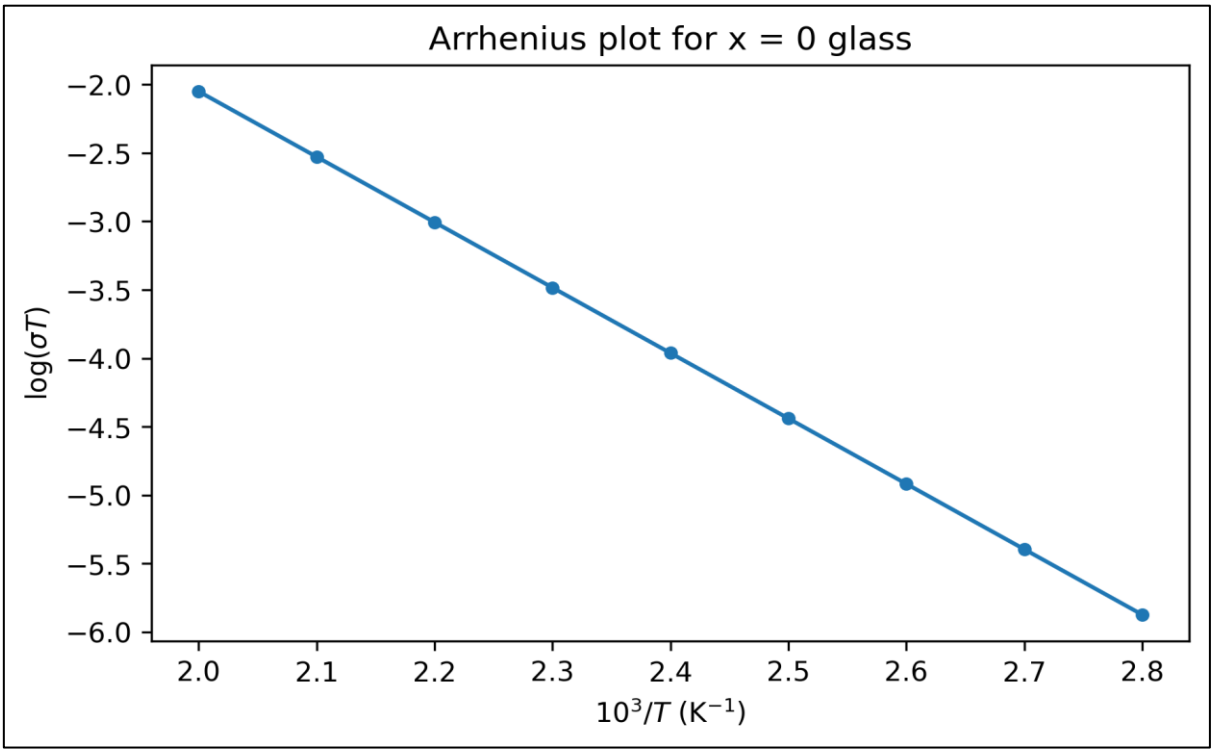


Fig 4 Arrhenius Plot [log(σT) vs. $10^3/T$] for the Unmodified (x = 0) Glass Composition, Slope = 4.78085, $E_a$=0.948eV.

ISSN No:-2456-2165 https://doi.org/10.38124/ijisrt/26aug1621

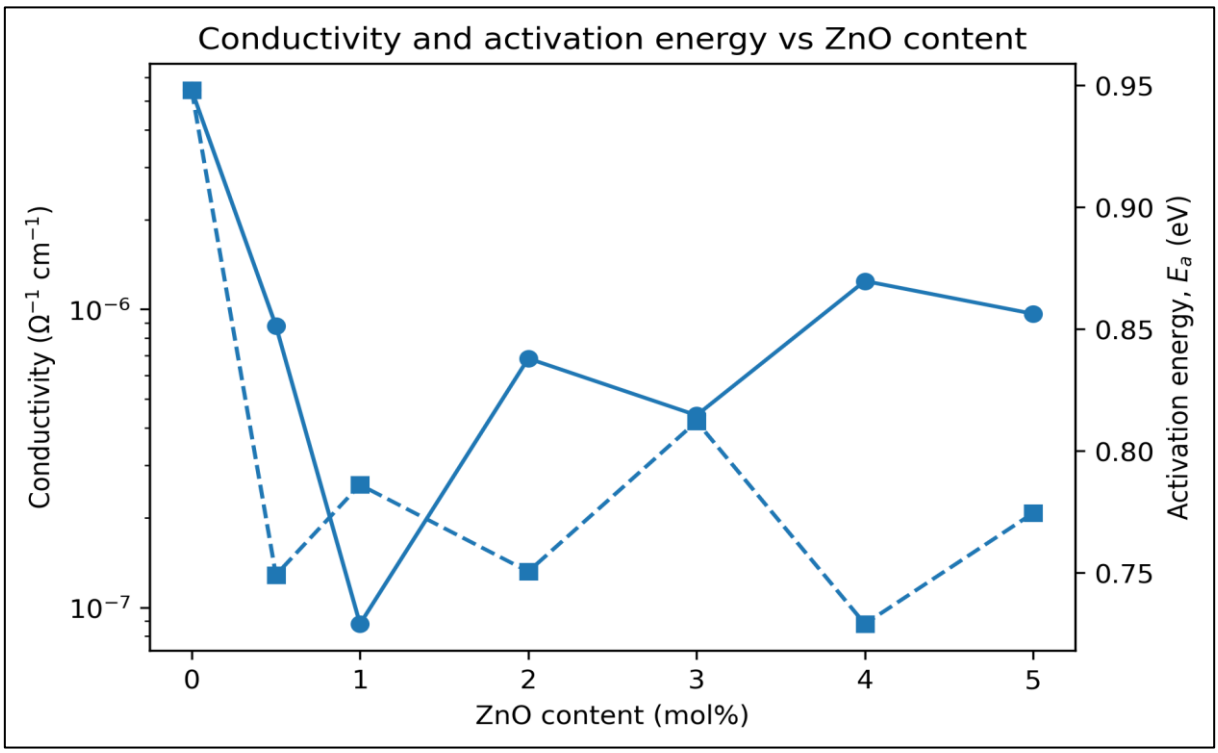


Fig 5 Ionic Conductivity at 200°C (Left Axis) and Activation Energy (Right Axis) of 42.5Na2O:(57.5-x)P2O5:xZnO Glasses as a Function of ZnO Content.

➢ *Mixed-Modifier Interpretation*

The non-monotonic dependence of conductivity on ZnO content, together with the corresponding variation in activation energy, is consistent with a mixed-modifier effect associated with the coexistence of $Na^+$ and $Zn^{2+}$ environments. Mixed-modifier studies of phosphate glasses show that replacing one modifier species with another can generate non-linear changes in physical properties because different cations prefer different local structural environments and migration pathways [5–7].

The present trend is also relevant to earlier mixed-alkali zinc phosphate glasses, in which extrema in dc conductivity and activation energy were reported as the ratio of dissimilar alkali modifiers was varied. That work attributed the transport anomaly to an energy mismatch between different cation sites and to disruption of preferred migration pathways [7]. More recent studies of sodium-containing phosphate glasses have likewise reported non-monotonic conductivity and activation-energy changes when additional network-modifying or network-forming oxides are introduced [10,11].

The conductivity minimum near x = 1 mol% ZnO may therefore indicate a composition range in which the coexistence of $Na^+$ and $Zn^{2+}$ environments most strongly perturbs the pathways available to the mobile charge carriers. This interpretation is a hypothesis consistent with the observed transport trend rather than a direct structural proof. Direct evidence of cation coordination and phosphate-network rearrangement would require complementary techniques such as Raman spectroscopy, FTIR, solid-state NMR, XPS or impedance spectroscopy.

A further limitation is that the present measurements were obtained with an LCR-Q meter at a single operating frequency rather than by broadband impedance spectroscopy. Related $Na_2O$-modified zinc phosphate glasses have been shown by broadband measurements to exhibit composition- and frequency-dependent ionic, polaronic and mixed conduction [12]. Accordingly, the present results should be described conservatively as electrical conductivity at the measurement frequency. A rigorous separation of dc ionic, electrode-polarization and electronic/polaronic contributions cannot be established from the present dataset alone.

## IV. CONCLUSIONS

Ternary sodium phosphate glasses with ZnO contents between 0 and 5 mol% were prepared by the melt-quenching technique. The presented XRD patterns for x = 0.5 and 3 mol% ZnO exhibit broad diffuse halos without sharp Bragg reflections, consistent with amorphous glass formation. Temperature-dependent resistance measurements yielded an Arrhenius-type description of the electrical transport within the measured range.

At 200 °C, the reported conductivity varies non-monotonically with ZnO content, decreasing from $5.434 \times 10^{-6}\ \Omega^{-1}\ cm^{-1}$ for x = 0 to a minimum of $0.088 \times 10^{-6}\ \Omega^{-1}\ cm^{-1}$ at x = 1 mol%, increasing to $1.244 \times 10^{-6}\ \Omega^{-1}\ cm^{-1}$ at x = 4 mol%, and then decreasing at x = 5 mol%. The activation energy varies from 0.948 to 0.7289 eV and broadly follows the opposite trend. These results are consistent with a mixed-modifier effect associated with $Na^+$ and $Zn^{2+}$ environments, but the microscopic mechanism cannot be established conclusively without direct structural and frequency-resolved electrical measurements.

ISSN No:-2456-2165 https://doi.org/10.38124/ijisrt/26aug1621

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