Study of Li$^+$, Na$^+$ and Ag$^+$ ion conductivity and relaxation mechanism in Boro-Phosphate Glass system

SYNOPSIS OF THE THESIS TO BE SUBMITTED

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Ms. Vaishali Apurva Adhwaryu
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Under the direction, guidance and supervision of

PROF. D. K. KANCHAN

Solid State Ionics & Glass Research Laboratory
Department of Physics, Faculty of Science
The M. S. University of Baroda
Vadodara - 390002 (Gujarat) India

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INTRODUCTION:

Solid **S**tate **I**onics **(SSI)** is an interdisciplinary branch of **S**olid **S**tate **P**hysics that focuses on the study of ionic solids that exhibit a wide range of ionic conductivity, with values ranging from 10^{-13} S cm^{-1} to 10^{-1} S cm^{-1} [1], [2]**.** The material regarding Solid State Ionics is called **S**olid **S**tate **E**lectrolytes **(SSE)** and are also known as the terms **S**uperionic **C**onductors **(SC/SIC)** and **F**ast **I**onic **C**onductors **(FIC)** with ionic conductivities of the order of 10^{-5}-10^{-1} S cm^{-1}, which are comparable to those liquid electrolytes. Solid Electrolyte materials, which are electrical insulators given the fact that electrical conduction is primarily governed by ***ion*** **(cation/anion)** transport**.** Superionic solids present an enormous opportunity and scope in the burgeoning field of SSI because they are promising candidates for electrochemical devices such as batteries, fuel cells, and supercapacitors for energy storage; pacemakers; gas and pollutant sensors; electrochromic/smart memory windows/displays; Coulometers; and analogue potential memory devices [3].

The material or system that acts as a solid electrolyte (SE) should have the following key feature.

i. The ion conductivity of the system should be of the order of $10^{-3}\ S\ cm^{-1}$, which should be greater than the electronic conductivity (approx. 0.01% of the ionic conductivity) of the system.
ii. The energy barrier must be less than $1\ eV$ to facilitate ion migration.
iii. In order for the material to be appropriate for electrochemical applications, both its physical and chemical compatibility must be suitable.

Solid **S**tate **I**onics is an interdisciplinary study that includes aspects of physics, chemistry, and engineering. It encompasses concepts such as theory, the synthesis of material, characterizations of physical, thermodynamic, and structural properties, as well as potentially useful applications of the material. The backbone structure of the SSI system helps to facilitate the transfer of charged matter (ions) over the macroscopic distance in a system.

Solid electrolytes that exhibit ionic conductivity can be classified according to their backbone structures. These solid electrolytes include glass (amorphous) electrolytes (GE), polymer (PE)/gel polymer (polycrystalline) electrolytes (GPE), composites, and NASICONs (crystalline / polycrystalline).

Among these, glassy electrolytes have received a lot of attention because of their advantageous features, such as the absence of grain boundary regions, the ease of forming glass with the desired shape and size, and the isotropic way of conduction, which makes glass an ideal solid electrolyte for electrochemical devices [3]. Glasses have been made from inorganic minerals such as silica sand(SiO_2), sodium and calcium carbonates ($Na_2CO_3/CaCO_3$), feldspars ($KAlSi_3O_8/NaAlSiO_3/CaAl_2Si_2O_8$), borates ($B_2O_3$), and phosphates ($P_2O_5$) that melt and solidify into transparent glassy solids since ancient times.More than 90% of glass is made up of oxides, most notably silica, which is why the phrase "glass is sand and ashes" is sometimes used. Various organic chemicals such as halides, nitrates, sulphides, and chalcogenides are also used in the production of modern glass. Unlike crystalline materials, glasses have a local or short-range structure, a medium-range structure, and a long-range structure. However, long-range order is absent in glasses due to the lack of periodicity in structure. Therefore, diffraction experiment is required to determine the structure of a glass. Diffraction and other spectroscopic and thermal characterization techniques are needed to gain useful structural information from glasses.

For example, zinc phosphate and lead borate glasses are utilized as solders, whereas phosphate and fluro-phosphate glasses are used as laser hosts. Switching behavior and memory panel production both benefit from the usage of various chalcogenide glasses. Photocopiers have become an integral part of today's industries, and glassy selenium (Se) was at the forefront of their development. There is current interest in finding a replacement for silica fibers in IT field that uses halide glasses, which are more transparent. Amorphous Si and InCuSe are two examples of photovoltaic materials. Different ionically conducting glasses, especially Li and Ag based ones, are used in battery production. Ionic glass, also known as glassy electrolyte material, is a non-crystalline ionic solid that is formed when a molten liquid undergoes rapid cooling.

In general, the structure of ionic glasses renders them electrically insulating, and their conductivity is on the order of 10^{-12} S cm^{-1}. However, the composition of the glass can be altered to achieve high levels of ionic conductivity.

Glass can be created by combining a range of chemically-bonded components, including elements, simple chemical compounds, complex organic molecules, salt combinations, and alloys. There are a variety of methods, both ancient and modern, for creating glass from molten components. Sol-gel, evaporation and rapid quench techniques are examples of such procedures. As long as the material is capable of producing glass, any of the procedures used to form glass can be implemented.

To use oxides in the formation of ion-conducting glass, the crystallochemical postulates given by Zachariasen and Goldschmidt's radius ratio requirement must be met. Zachariasen formulated a set of general guidelines for the formation of glass frameworks, which are now known as Zachariasen's rule for glass formation[4]. Goldschmidt was the first to organize the glass formation criterion that emphasizes the importance of the ionic radius ratio in glass-forming oxides [5].According to the concept, the synthesis of glass is thought to require three fundamental components: glass network former, network modifier, and dopant salt. The structural units of the network-forming oxides $(SiO_2, B_2O_3, P_2O_5, GeO_2)$ are coupled with one another by 'Bridging Oxygen,' or BO, whereas the role of the modifier $(M_2O: Li_2O, Na_2O, K_2O, Ag_2O \text{ and } MO: CaO, BaO \text{ etc.})$ is to provide open structure via the formation of 'Non-bridging Oxygen,' or NBO, of the host glass matrix, and the additive $(MX;\ X = I, F, Br, Cl)$ metal halide salt facilitates decoupled ions, which results in ion conductivity in the glassy state of the material. Further classification of ion conducting glasses is dependent on the number of oxides utilized in glass formation: glasses with single glass former $(SiO_2\ /B_2O_3\ /P_2O_5)$, and mixed glass former $(MGF: B_2O_3\text{-}SiO_2, B_2O_3\text{-}P_2O_5)$.

Lammert and Heuer [6] revealed the occurrence of conductive routes in lithium silicate glass and suggested that the total amount of oxygen molecules serving as bridges has a substantial impact on the mobility of lithium ions at a single location. Sen and Mukherjee [7] observed that the activation energy for DC conductivity dropped logarithmically as mobility and concentration increased. The continuous random network (CRN) of silica implies that the directionality of the Si-O bond is quite strong. Due to the high degree of integration, the mass transport characteristics are exceedingly poor, indicating a high viscosity. The addition of alkali oxide (modifier) enables BO_3 to be changed to BO_4, however over a specific threshold, considerable depletion (reconversion of BO_4 to BO_3) is observed, which is correlated with a boron anomaly. In borate glasses, the modifier concentration is critical. Rao et al; have reported that the compositional alkali oxides influence the characteristics of binary glasses containingB_2O_3. The formation of NBOs occurs at the expense of BOs when network-modifying alkali oxides are added to the phosphate glass matrix. Alkali oxide M_2O depolymerizes the phosphate network in the host matrix. Adding alkali and alkaline earth oxides changes the ultra-phosphate tetrahedral unit into a polymer-like linear chain of metafollowed by pyro- and then ortho-phosphate unit. Alkali oxide lowers activation energy and boosts ionic conductivity. Additional NBOs weaken glass network connectivity, easing cation transport[1]. Martin et al; have found that the conductivity of sodium borosilicate glasses it appears to be controlled by the glass network getting denser and stronger, which has a positive Mixed Glass Former Effect (MGFE) [9]. In the $SiO_2 - B_2O_3 - R_2O\,; R = Li,\ Na,\ K,$ $or\ Cs$ glass system, the size of the alkali atoms changes the structure of the glass, which in turn changes the macroscopic properties of the glass, most notably its electrical conductivity and glass transition temperature. It has been demonstrated that the addition of B_2O_3 to a phosphate network improves its thermal and mechanical stability, as well as its electrical properties. Borophosphate glass possesses characteristics unique from those of pure phosphate and borate glasses. Chemical durability can be extended by substituting P_2O_5 for B_2O_3 or by mixing the two, which transforms the three-dimensional structure of metaphosphate glass into the three-dimensional structure of borophosphate glass. It was demonstrated by Chiodeli et al; that the borophosphate glass group is made up of connected PO_4 and BO_4units that share a negative charge that is provided by the oxide modifier [10]. The mixed glass network effect (MGFE) is observed in sodium ion conducting borophosphate glass system$Na_2O - B_2O_3 - P_2O_5 - GeO_2$, where it leads to a significant increase in electrical conductivity. To a similar extent, the conductivity of Ag^+ in the mixed glass former system i.e. $AgI - Ag_2O - B_2O_3 - P_2O_5$ has also been investigated. Lithium borophosphate glasses have higher DC conductivity (σ_{dc}) than binary phosphate and borate glasses. Munoz et al; argued that lowering the average $Li - Li$ distance increases Li^+ ion mobility [11].

Different types of glasses show varying magnitude of conductivity enhancement, suggesting that the sensitivity of ion transport to differences in network unit structure is system-specific. Interestingly, from numerous studies that when an additive dopant salt - the majority of which is halide and sulfate-based, is added to the glass matrix, it appears to dissolve into the structure and fill its interstices. As a result, the network expands without affecting its parent glass structure, allowing better ion migration so that the electrical properties evolve.

The solid-state ionic glass works as an electrolyte in electrochemical devices such as fuel cells, supercapacitors, solid-state batteries, and electrolyzer-like electrochemical devices. For the process of electron beam recording and a memory device called memristor-capable of operating at very high speed ($< 10\ ns$) through electro-migration of cation or anions are also possible using solid-state ionic materials [10].

It is still early to investigate and understand how different metal halides function as dopant salts in the mixed glass former network in order to comprehend ion dynamics for the ion transport mechanism. In other words, comparing metal halide salts in borophosphate glassy solid electrolytes to reveal the underlying mechanisms of ion dynamics is still to move on.

With the present thesis, the ultimate objective of the research was to gain a comprehensive understanding of the ion conduction mechanism in glassy electrolytes containing metal halide salts in a homogeneous mixed glass former framework and then apply this understanding to discover and optimize the physical properties of materials. The primary goal of presented thesis is to ***"Study of Li^+, Na^+ and Ag^+ ions transport and relaxation mechanism in Boro-Phosphate Glass system".***

Present Thesis Work:

The present thesis focuses on the preparation and characterization of borophosphate glass electrolyte, which supports / controls the Li^+, Na^+ and Ag^+ ion migration in the glass structure depending on glass composition.In contrast to the separate pure phosphate and borate glasses, borophosphate glass possesses unique properties. By changing the phosphate for borate or combining the two, the borophosphate glasses are transformed from the linear-chain structure of metaphosphate glass to the three-dimensional structure of borophosphate glass, helping to increase their chemical durability.

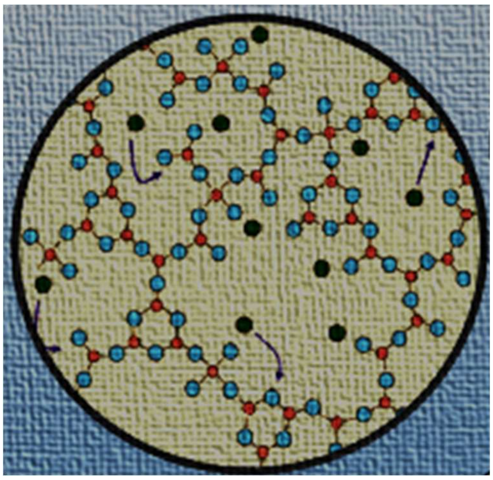

Figure 1: Key components of glass composition

For the current study, the boro-phosphate glass series with ternary stoichiometry has been studied and analyzed. Network former (borate-phosphate units), network modifier (metal oxide), and dopant-additive (metal halide) salt are the key components of the examined boro-phosphate glass composition as depicted in Fig.1.

🔴 $B_2O_3 - P_2O_5$ glass skeleton 🔵 BO and NB ● Mobile cation – $Li^+/Na^+/Ag^+$

Three alternative metal oxide-modified compositions have been added to the borophosphate matrix in order to get the desired outcomes while preparing the glass series necessary to accomplish the objective. It has been observed that the Metal Iodide (MI) dopant salt has a role in modifying the electrical and physical properties of metal oxide-modified boro-phosphate glass formations. Here, we follow the general formula for the ternary borophosphate glass system.

$$\boldsymbol{MI - [M_2O - (B_2O_3 - P_2O_5)];\ where\ M = Li/Na/\ Ag}$$

The compositional boro-phosphate glass series are as follows,

Series (a): LBP: $x(LiI): (100 - x)[(60\, Li_2O: (8\, B_2O_3 - 32\, P_2O_5)]$

$where, x\ varies\ from\ 5\ to\ 25, with\ interval\ of\ 5.$

Series (b): NBP: $x(NaI): (100 - x)[30\, Na_2O: (56\, B_2O_3 - 14\, P_2O_5)]$

$where,\ x = 1, 2.5,\ 4, 5, 10, 15, 20$ wt.%

Series (c): ABP: $x(AgI): (100 - x)[30\, Ag_2O: (56B_2O_3 - 14\, P_2O_5)]$

$where,\ x = 0, 1, 3, 5, 7$ wt.%

THE OBJECTIVES OF THE PRESENT WORK

1) To prepare glass electrolytes using the traditional melt quenching process.
2) To investigate the influence of metal iodide variation on the structure, surface morphology, and thermal properties of the boro-phosphate glasses using XRD, SEM, FTIR, and TG-DTA etc.
3) Use of Electrochemical Impedance Spectroscopy to investigate the electrochemical properties of the glass electrolyte samples.
4) A comparison of electrochemical parameters and relaxation dynamics to establish the ion dynamics model for each ion viz., Na, Li & Ag due to metal halide doping in the boro-phosphate glass systems.

The current thesis incorporates seven chapters to illustrate the entire research study.

CHAPTER 1: INTRODUCTION & LITERATURE SURVEY

This chapter discusses the history of the Super Ionic Conductor (SIC) and its basic overview with the classification of such materials. Fast Ion Conductor (FIC/SIC) has the potential to be utilized as the Solid Electrolyte. The chapter contains a comprehensive description of glass electrolytes and a classification according to their main components of ionic glasses. An exhaustive discussion of the main features, including the development of the glass network, the modifier followed by the dopant salt, is also a part of this chapter.

CHAPTER 2: MODEL FOR ION TRANSPORT IN GLASSES

For an ion conduction process to occur in an amorphous system, several models and theories incorporating bulk conductivity, relaxation behavior, and other aspects have been proposed by numerous researchers. This chapter discusses the fundamental attributes of superionic conduction, theoretical models with the essential schematic and mathematical operations to comprehend the ion conduction mechanisms, and the general characteristics of charge transport in glasses.

CHAPTER 3: MATERIAL PREPARATION & CHARACTERIZATION TECHNIQUE

This chapter illustrates the row materials, preparation method and characterization techniques to understand the glassy electrolyte system in detail. For the preparation of glassy electrolytes, a technique known as quick melt quench was selected as the appropriate method. The chart present in this chapter gives more information regarding the preparation technique. The physical characterization techniques, including X-ray diffraction (XRD), Fourier Transform infrared spectroscopy (FT-IR), Scanning Electron Microscopy (SEM), and Thermo-Gravimetric Analysis (TG-DTA), are described to determine the structural, morphological, and thermal profile respectively for the prepared samples. A series of experiments have been conducted using Electrochemical Impedance Spectroscopy (EIS) tool to investigate electrical and electrochemical behaviors of glass electrolytes.

CHAPTER 4: Physical, Structural, Thermal and Electrical Properties of Lithium Borophosphate Glass series (LBP)

This chapter describes the Structural, Physical, Thermal and Electrical properties of $x(LiI){:}\,(100-x)[(60\,Li_2O{:}\,(8\,B_2O_3-32\,P_2O_5)]$, with x =0 to 25 wt.%. X-ray Diffraction pattern, obtained at room temperature, has been considered to confirm the amorphous nature of all prepared glass samples. According to the findings of FTIR study, incorporation of LiI into Boro-Phosphate glasses results in the progressive polymerization of borate while simultaneously causing the depolymerization of the phosphate network.IR studies also indicate that most of the units of glass formers move to a lower wave number. It is because BO_3units change to BO_4units and PO_4 units transform to PO_5 units, which yields the expansion of the glass structure. The values of different physical parameters like density (ρ), molar volume (V_m), Oxygen Packing Density (OPD), and the glass transition temperature (T_g) have been determined. The conductivity analysis shows that with the addition of LiI, the DC conductivity increases, and the corresponding activation energy decreases due to a reduction in both the electrostatic binding energy and the strain energy required for the simple passage of the lithium. The nature of the borate framework structure is rigid, which may account for the modest/ very slight variation in glass transition temperature observed. The relaxation activation energies for the glass series have been derived and presented. In the prepared glass electrolytes, the relaxing mechanism of ions exhibits a Non-Debye nature, manifested through the Nyquist plot. The temperature-dependent dc conductivity follows the Arrhenius equation, indicating thermally stimulated lithium ion transport. The activation energies for conduction and relaxation were almost identical for the present glass series, which was found by studying ion relaxation using the conductivity and relaxation formalisms. This finding suggests that the charge carrier (Li) ions overcome the same energy barrier when conducting and also at the time of relaxing. Additionally, using the enthalpy of carrier migration(H_m), Coulombic (effective) barrier height (U_H) and Fermi energy (E_f) have also been estimated for the charge carrier dynamics to comprehend the glass series effectively. The variation of power law exponent $n(T)$ and distance between Li-Li ions R_{min} values estimated theoretically and experimentally obtained concluded that Li^+ ion transport happens according to the Correlated Barrier Hopping (CBH) mechanism in the current glass system.

CHAPTER 5: Physical, Structural, Thermal and Electrical Properties of Sodium Borophosphate Glass series (NBP)

The Structural, Physical, Thermal and Electrical Properties of $x(NaI):(100-x)[30\ Na_2CO_3:(56\ B_2O_3-14\ P_2O_5)], x=, 2.5, 4, 5, 10, 15, 20$ wt. % (LBP) glass series have been discussed in this chapter. All the prepared glass samples have been analyzed by XRD at room temperature, confirming their amorphous nature. In the middle of the infrared spectrum, FTIR spectra of NBP glasses exhibit considerable evidence of $B-O$ bonds in BO_4 tetrahedral. The increase in the intensity of this band reveals that BO_4 tetrahedra tend to form diborate clusters to fit large anions (I^-) into the boron oxygen network. $BO_4$is responsible for the sharp peak at 995 cm^{-1}, and the peak at 1076 cm^{-1} is associated with the vibration of stretching of the $B-O-B$ bond in the tetraborate group of BO_4 units.The observed maxima in the activation energy and minima in the glass transition temperature reveal the mixed glass former effect in the current glass series. The physical characteristics such as the density of the glass samples were determined using Archimedes principle. Using density values, the atomic distance between atoms, the molar volume, the oxygen packing density and the total number of Na cations have been computed. Complex Impedance Spectroscopy (CIS) is used to investigate the electrical properties of the current glass series wherein the Nyquist plot shows a significant deviation from the ideal Debye nature of the system. It is observed that with the addition of $NaI (wt.\%)$ to sodium oxide modified borophosphate glass system up to a certain extent, the dc conductivity increases, and the associated activation energy decreases, with a minimum value of $0.82\ eV$, which follows the Arrhenius trend. The variation of decoupling index and number of Fermi Energy states are in consonance of the conductivity results. The activation energy computed using frequency-dependent conductivity according to Jonscher's Power Law (JPL) and relaxation characteristics from modulus exhibited the same results of activation energy indicating that the energy required for an ion to overcome the energy barrier and ion energy for relaxation are same. For the current system, various scaling formalisms for conductivity and modulus have been incorporated to comprehend the behavior and its theoretical validity of it with the pre-defined models.

CHAPTER 6: Physical, Structural, Thermal and Electrical Properties of Silver Borophosphate Glass series (ABP)

This chapter illustrates the Structural, Physical, Thermal and Electrical properties of $x(AgI):(100-x)[30\, Ag_2O:(56B_2O_3-14\, P_2O_5)]$ with $x = 0, 1, 3, 5, 7\ wt.\%$ present in the prepared glass series. XRD, one of the structural characterization techniques, was used to establish that the glass electrolyte samples prepared by the melt quench procedure have an amorphous composition. FTIR has been used to analyze the various vibrational modes of structural building blocks and the type of chemical bonding formed between them. The deconvoluted IR spectra in the wavenumber range $1300-1500\ cm^{-1}$ reveal newly formed PO_4^{3-}molecules and $P-O-B$ linkage in the glass system with the addition of AgI salt.It was possible to infer the molar volume, cation concentration, and inter-atomic distance from the determined density (ρ)value.The glass transition temperature (T_c) varies as a function of glass compositions, owing to a decrease in glass structure rigidity and an increase in the number of non-bridging oxygen. Complex Impedance Spectroscopy (CIS) of the electro-material demonstrates the formation of double layers of the capacitor as the consequence of charge accumulation at the electrode-electrolyte interface. The analysis of the plot of $log\sigma_{dc}$ versus$1000/T$, which was of a linear trend, suggests the ion hopping mechanism for conduction exhibits Arrhenius behavior. The silver ion released from the AgI compound behaves as a modifier, which promotes the formation of non-bridging oxygen groups in the backbone network.According to conduction behavior; the silver iodide in the silver borophosphate glass follows the Anderson-Stuart (A-S) model. After a certain amount of AgI in the silver boro-phosphate glass, Ag^+ ions start changing their local coordination from oxygen to an I^- environment, resulting in a decrease in conductivity or an increase in activation energy. The decoupling index (R_τ), mobile ion concentration (K'), and power law exponent $n(T)$ indicate a correlation between the composition of the glass. The modulus formalism represents the relaxation process that takes place in superionic glasses as a result of the motion and relaxation of ions. The electric modulus curve provides the stretching parameter(β) equivalent to the full width at half the maximum (FWHM) value yielding the Non-Debye nature of the curve. From the modulus studies, the time required for relaxation (τ_c)as a function of the inverse of the temperature scale $(1000/T)$ was evident with a good approximation of the Arrhenius behavior. All dynamic processes, regardless of temperature or composition of the glass, exhibit slight variation in activation energy and disturbance of relaxation durations, evidenced by the scaling of conductivity and electric modulus. The nearly perfect superposition of the conductivity spectra at various temperatures into a single master curve implies the existence of the Time-Temperature-Superposition (TTS) and temperature-independent conduction process.

CHAPTER 7: Comparison of Investigated series and Conclusion

This chapter depicts the comparative study of samples of all three glass series ABP, NBP and LBP. We aim to investigate the influence of various metal halides with varying proportions within the metal oxide-modified Boro-phosphate glass systems. This chapter concentrates on the physio-chemical properties of the main components of ionic glass, such as network former, network modifier, and the most significantly dopant-metal halide salt, which governs the phenomenological properties of glass electrolyte.

THE PLANNED INDEX CONTENT OF THESIS

1. INTRODUCTION to Solid Electrolytes- Superionic / Fast Ionic Conductor (SIC/FIC) and Solid State Ionics (SSI)

2. MODEL FOR ION TRANSPORT IN GLASSES

3. MATERIAL PREPARATION & CHARACTERIZATION TECHNIQUE

4. PHYSICAL, STRUCTURAL, THERMAL AND ELECTRICAL CHARACTERIZATION OF LITHIUM BOROPHOSPHATE GLASS DOPED WITH LITHIUM IODIDE (LBP)

4.1. INTRODUCTION TO THE GLASS SERIES:

$x(LiI):(100-x)[(60\ Li_2O:(8\ B_2O_3-32\ P_2O_5)]$

4.2. EXPERIMENTAL

4.3. PHYSICAL CHARACTERIZATION

4.4. STRUCTURAL CHARACTERIZATION

4.5. THERMAL CHARACTERIZATION

4.6. ELECTRICAL CHARACTERIZATION/IMPEDANCE SPECTROSCOPY

4.7. CONCLUSION

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$x(NaI):(100-x)[30\ Na_2O:(56\ B_2O_3-14\ P_2O_5)]$

5.2. EXPERIMENTAL

5.3. PHYSICAL CHARACTERIZATION

5.4. STRUCTURAL CHARACTERIZATION

5.5. THERMAL CHARACTERIZATION

5.6. ELECTRICAL CHARACTERIZATION/IMPEDANCE SPECTROSCOPY

5.7. CONCLUSION

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$x(AgI):(100-x)[30\ Ag_2O:(56B_2O_3-14\ P_2O_5)]$

6.2. EXPERIMENTAL

6.3. PHYSICAL CHARACTERIZATION

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Adhwaryu

Prof. D. K. Kanchan (Retired)
Guiding Teacher & Motivator
Department of Physics,
Faculty of Science
The M. S. University of Baroda
Vadodara-390002

Ms. Vaishali Apurva Adhwaryu
Research scholar,
Solid State Ionics & Glass research laboratory
Dept. of Physics; Faculty of Science,
The M. S. University of Baroda
Vadodara-390002