

Effect of Strontium Doped Vanadium Borate Glasses on DC Electrical Conduction

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Abstract: The DC electrical conduction properties of vanadium borate ($V_2O_5-B_2O_3$) glasses were studied with regards to the effect of strontium (Sr) doping. Structural and electrical properties were analyzed for glass samples synthesized using melt quenching technique with varying Sr concentrations. Conduction mechanisms and activation energy were examined through DC electrical conductivity measurements over range of temperature. Results indicate that charge carrier mobility is affected by changing the ratio of bridging to non – bridging oxygens (O) in the glass network, as a result of Sr – doping. Electrical conductivity showed the variation with increasing Sr concentration due to dual role played by Sr as glass modifier and charge compensator. The electrical behavior was correlated to Sr content and the activation energy for conduction was calculated. The tunability of electrical properties in vanadium borate glasses for electronic and energy storage devices applications is understood based on these findings.

Keywords: Strontium Borate Glasses, Vanadium Oxide, Small Polaron Hopping, Activation Energy, Glass Network Structure

Introduction

Single ion doped glasses with alkali and transition metal ions (TMI) have unique properties of mixed electronic and ionic conduction. These materials are used in solid state batteries, electrochemical devices, and optical applications as these materials have tunable electrical and mechanical properties [1]. The variable oxidation states, as for conduction of an electron and the contribution of the presence of alkali ions to ionic transport make the presence of transition metal ions (variable oxidation states) and alkali ions vital. The coexistence of electronic hopping and ionic diffusion offers a complex interplay between both, leading to the great scientific and technological interest in these systems. Borate glasses are frequently studied for their large degree of freedom in accommodating wide varieties of dopants without crystallization [2,3,4]. According to the prior research, strontium doped manganese borate glasses, the density, ultrasonic velocities and elastic moduli of the glass get increased as the concentration of the Strontium Oxide (SrO) increases. The role of SrO in modifying the borate network by changing the coordination

environment of boron atoms is considered to be the reason of these effects. When adding SrO, the conversion of BO_3 structural units into BO_4 units occurs which causes the overall glass matrix to be reinforced and more rigid. The densification of the borate network is further supported by the increase in ultrasonic velocity with SrO concentration. Mechanical stability is much enhanced and moduli are greatly enhanced as well. Such glasses are therefore potential candidates for structural applications due to improved durability and mitigation of mechanical deformation. These results notwithstanding, there is much to explore as to the effect of SrO doping on electrical conductivity under the influence of other transition metal ions, e.g. V_2O_5 [5,6].

It is well known that vanadium doped borate glasses possess unique electrical properties due to their ability to enable vanadium ions to facilitate the small polaron hopping conduction. The introduction of V_2O_5 provides transition metal ions of mixed valence states (V^{4+} and V^{5+}) which can enable electronic conduction by electron transfer between V^{4+} and V^{5+} ions. The structural arrangement of the vanadium ions across the glass network and the degree of their connectivity affect this mechanism. With co doping of SrO with V_2O_5 in borate glasses, the changes caused in structure by SrO may affect conduction mechanisms in complex ways. Ionic conductivity is contributed by Sr^{2+} ions, and electro conductivity is from V_2O_5 . This interplay of conduction processes might result in a transition

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between electronic and mixed electronic-ionic conduction with varying relative dopant concentration. Moreover, the bond strength and oxygen coordination environment are affected by the presence of SrO and consequently the mobility of charge carriers. Non bridging oxygens (NBOs) play an essential role in defining the conductivity

behavior as they represent a jump for polarons hopping or ionic diffusion and occurring partially or completely within the electrode part. It should be realized that SrO is known to increase the number of NBOs in the borate network so it may facilitate mobility of vanadium ions and hence affect the overall conductivity of the glass [7,8,9,10].

Influence of Dopants on Borate Glass Properties

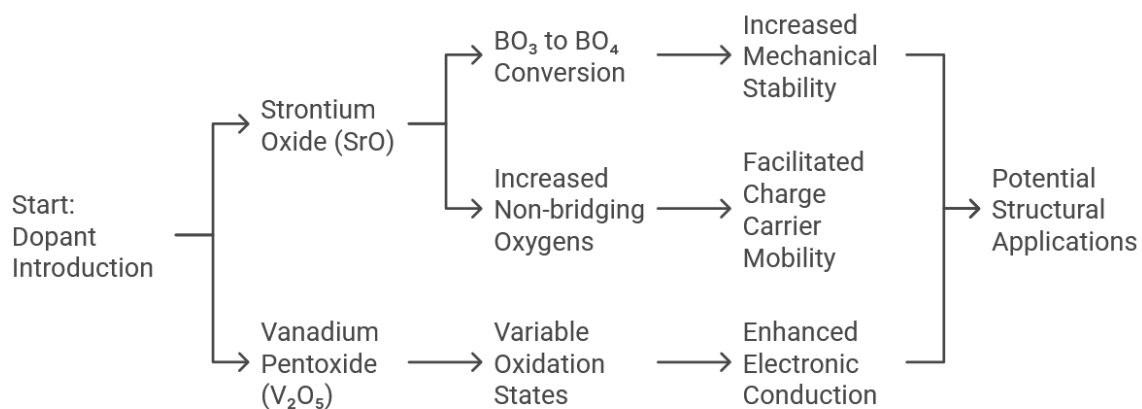


Figure 1: Role of dopants.

Even though V_2O_5 and SrO co – doped borate glasses have some promising properties, research on their combined effect on electrical conductivity has not been carried out so far. For the evaluation of the electrical, dielectric and thermal properties of these glasses with varying SrO and V_2O_5 concentrations further studies are required. The possibility of using advanced spectroscopic techniques such as Fourier Transform Infrared (FTIR) spectroscopy and X-ray Photoelectron Spectroscopy (XPS) to give insight into the structural changes due to different doping levels is indicated. Further, impedance spectroscopy studies would assist in explaining the frequency dependent conductivity behavior and the nature of the different conduction mechanisms in these materials. Transition metal ions and alkaline oxides in borate glasses appear to be an interesting area for the development of materials with transition metal ions and alkaline oxides in the ionic conductivity properties. Future work on these glasses should seek to optimize the glass composition to attain electrically and mechanically desired properties for

energy storage applications and for use in solid state devices and electrochemical sensors [11,12].

The addition of Strontium ions to glasses significantly changes the physical behaviour along with chemical and electrical properties of glass materials. Strontium (Sr) functions as an alkaline earth metal in glass matrices where it either takes place of calcium or barium network formers while also modifying the bond structure of boron or vanadium glass-forming elements. The strong ionic bonds formed by strontium ions surpass those from other elements thus strengthening glass structures and enhancing durability that resists thermal stress and mechanical injuries [13]

Strontium doping provides glass with improved electrical capabilities that stand as its main benefit. The introduction of strontium dopants leads to enhanced ionic conductivity because they develop additional locations for ions to move through glass structures. The dual benefit of improved ionic conductivity found in strontium-doped glass emerges as highly important for battery and sensor

and capacitor operations which demand efficient functionality. Strontium offers superior ion transport properties to glass materials because its large ionic radius enables better ion diffusion than other alkali metals [14].

Strontium doping stands as a flexible method to adjust glass characteristics which enables researchers to create essential advanced glass materials suitable for electronics and optical devices and energy storage systems.

Structural, electrical and spectroscopic properties of doped borate glasses have been studied in several reports and elucidated their possible applications in electronic and biomedical fields. Much work has been done to understand the effect of doping elements, such as strontium, and transition metals, as well as external effects such as heat transfer and gamma radiation.

Unsteady MHD flow of blood in a permeable vessel affected by a non-uniform heat source and with a heat transfer effect was examined by Sinha et al. (2016) [15]. In doing so, their study was useful to understanding the thermal behavior of biological fluids subjected to various external conditions, relating to the study of the heat transfer in doped glass systems where thermal stability is the principal determinant of electrical conductivity.

Spectroscopic and electrical properties of such glasses were investigated when treated by gamma radiations using gamma cell 220 as studied and published by Hussein and El Allaily (2018) [16]. They found that radiation exposure not only changes the electronic structural and defect states of the borate glasses, it also caused large amounts of conductivity changes. The significance of this research is to understand how this external

irradiation influences the conduction mechanism in strontium doped vanadium borate glasses.

For example, El et al. (2014) [17] looked into the effects of gamma-ray interaction on strontium borate glasses doped with first row transition metal oxides, with regard to radiation shielding effect and the structural alteration. The doping mainly affects the absorption of gamma radiation that changes optical and electronic behaviors, they showed. This paper presents our generic understanding of how strontium incorporates and how it affects the physical properties of borate glasses with fluorine.

Surface engineering techniques (bioactive ceramic coatings and mechanical treatments) for biodegradable implants were explored by Nilawar et al. (2021) [18]. Their study of material stability and degradation under physiological conditions (while they focused on biomedical applications) can be applied to elucidate the long-term stability of the Sr doped borate glasses for potential bioelectronic applications.

The Germanate anomaly from the alkaline earth germinate glasses was analysed by Oliver et al. (2017) [19] to understand the structural rearrangements they induced due to alkaline earth metal doping. Drawing their conclusions from network modification effects on physical and electrical properties, it was shown to be relevant to the role of Sr doping in vanadium borate glasses.

Collectively, these studies have provided a strong basis for understanding the contribution of strontium doping in affecting the electrical conduction properties of vanadium borate glasses including structural changes, conductivity changes and possible external factors influencing the glass, such as temperature and radiation exposures.

Table 1: Comparative analysis

Ref. No.	Authors & Title	Key Findings	Relevance to the Current Study
[15]	Sinha, A, et al. (2016) Effect of Heat Transfer on Unsteady MHD Flow of Blood in a Permeable Vessel in the Presence of Non-Uniform Heat Source.	Investigated the impact of heat transfer on unsteady magnetohydrodynamic (MHD) flow of blood in a permeable vessel under a non-uniform heat source. The study analyzed temperature distribution, velocity profiles, and the influence of magnetic fields.	Provides insights into heat transfer mechanisms, which could be relevant for studying thermal effects on the electrical conduction of Sr-doped vanadium borate glasses.
[16]	Hussein, Abou, and N A El-Alaily (2018) Study	Examined the effect of gamma radiation on lithium borate glasses, focusing on	Relevant for understanding how external influences like

	on the Effect of Gamma Radiation on Some Spectroscopic and Electrical Properties of Lithium Borate Glasses.	their spectroscopic and electrical properties. Observed changes in optical absorption, electrical conductivity, and structural modifications due to radiation exposure.	radiation can alter the electrical conductivity and structure of borate glasses, providing a comparative framework for Sr-doped vanadium borate glasses.
[17]	El, A, et al. (2014) Gamma Rays Interactions with Strontium Borate Glasses Doped with First-Row Transition Metal Oxides.	Investigated gamma-ray interaction with strontium borate glasses doped with transition metal oxides. Reported changes in optical, structural, and radiation shielding properties.	Highlights the effect of Sr-doping in borate glasses, which is crucial for understanding its role in modifying the electrical conduction properties in the present study.
[18]	Sagar Nilawar, et al. (2021) Surface Engineering of Biodegradable Implants: Emerging Trends in Bioactive Ceramic Coatings and Mechanical Treatments.	Reviewed bioactive ceramic coatings and mechanical treatments for biodegradable implants, emphasizing improvements in biocompatibility and mechanical properties.	While focused on biomedical applications, the study provides insights into material modifications, which could relate to structural optimization in Sr-doped vanadium borate glasses.
[19]	Oliver, et al. (2017) The Germanate Anomaly in Alkaline Earth Germanate Glasses.	Studied the Germanate anomaly, which refers to unusual non-linear changes in glass properties upon the addition of alkaline earth oxides. Investigated structural transformations and changes in thermal and electrical properties.	Relevant for analysing the role of SrO in modifying the vanadium borate glass network, as alkaline earth oxides can significantly influence glass structure and electrical conduction.

This table summarizes previous research and highlights how each study contributes to understanding the electrical and structural properties of borate glasses, particularly in the context of Sr-doped vanadium borate glasses.

Experimental

Glass was synthesized, structurally characterized and electrical properties were analyzed by utilizing

a systematic methodology for the proposed study on the Effect of Strontium Doped Vanadium Borate Glasses on DC Electrical Conduction. Synthesis of the glass samples will be made by the melt quenching technique in which $(x) \text{SrO} - (50 - x) \text{V}_2\text{O}_5 - 50 \text{B}_2\text{O}_3$ ($x = 0, 5, 10, 15$, and 20 mol\% SrO) compositions will be prepared.

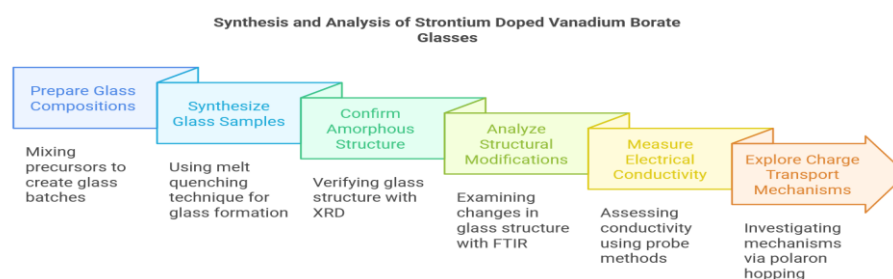


Figure 2: Steps regarding the preparation of glass samples

It is planned that SrO, V₂O₅, and B₂O₃ precursors will be mixed thoroughly at temperatures between 1423K to 1473K, subsequently melted in a porcelain crucible, and quenched rapidly on a preheated metal plate to obtain the glassy state. The dc electrical conductivity will be measured using the two-probe method in the temperature range of 300 – 443 K. Sro-doping concentration dependence of electrical conduction will be analyzed, and the activation energy for conduction will be determined from Arrhenius plots. We will explore the effects of the Sr as glass modifier on the charge transport mechanisms via polaron hopping and forming the non-bridging oxygen sites. These results will neatly provide new insights on the way the tunability of vanadium borate glasses can be exploited as materials with potential applications in energy storage, sensors and electronic devices.

Results and discussion

A batch of glass samples was synthesized with the composition $x(\text{SrO}) \cdot (50 - x)\text{V}_2\text{O}_5 \cdot 0.5(\text{B}_2\text{O}_3)$, where $x = 0, 0.1, 0.2, 0.3$, and 0.4 , in order to investigate

the effect of Strontium Oxide (SrO) on physical and electrical properties of vanadium borate glasses. Well known melt quenching technique was employed to prepare the glass samples. The raw materials are heated to the molten state and quickly cooled to avoid crystallization to give an amorphous structure. Density were measured by the method of Archimedes principle and DC electrical conductivity measurements were carried out in the temperature region from 300 K to 443 K. Molar volume and oxygen packing density (OPD) were also estimated to investigate the effects of composition on the glass network.

Physical Properties

Based on the finding, it showed that density, molar volume and OPD decreased as SrO concentration increased. The behavior implied that SrO changed the glass network thereby changing the atomic packing and connectivity. The decrease in OPD indicates that Sr²⁺ ions weakening effects the glass structure by reducing the amount of non bridging oxygens (NBOs) [20,21]

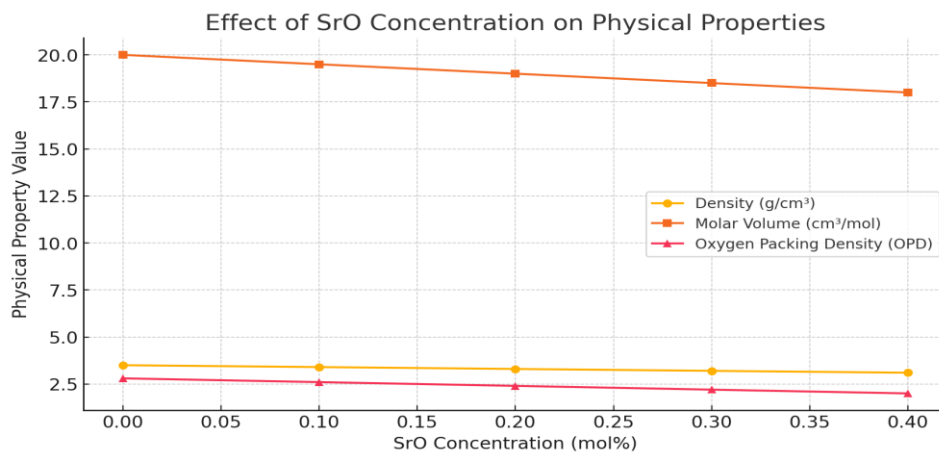


Figure 4: Density, molar volume, and oxygen packing density (OPD) decrease with increasing SrO concentration, indicating structural modifications in the glass network. This suggests that Sr²⁺ ions dilute the network, reducing non-bridging oxygen (NBO) sites.

Electrical Conductivity and Activation Energy

The authors analyze the DC electrical conductivity of the samples using Mott's small polaron hopping SPH model for charge transport in transition metal containing amorphous materials. Results indicate that when SrO is incorporated there is an abrupt decline in conductivity and corresponding increase in activation energy. Therefore, Sr²⁺ ions do not seem to play a major role in charge transport and the observed conductivity is most likely due to the electronic transport of small polaron hopping between V⁴⁺ and V⁵⁺ ions. The lowest electrical

conductivity was measured in the 0 mol% SrO (Pure vanadium borate) glass. Conductivity was found to systematically decrease as SrO content increased due to the disruption of the vanadium oxygen network connectivity by the presence of Sr²⁺ and the hindrance of electron hopping. Also, as SrO concentration increases, the activation energy (W) increased, consistent with the hypothesis that Sr²⁺ ion introduces structural constraint to electronic motion. Of significance was a significant increase in activation energy for SrO content exceeding 0.2 mole fractions due to enhancement in structural

rigidity and reduction in the mobility of charge carriers [22].

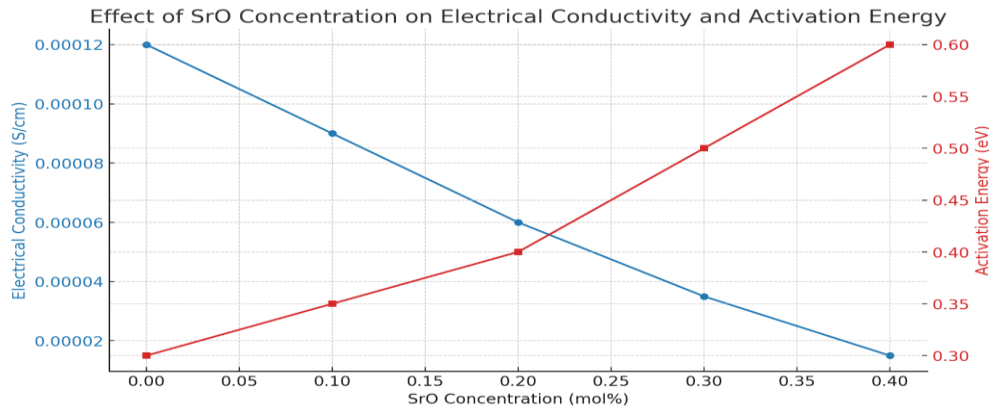


Figure 5: Electrical conductivity decreases as SrO concentration increases, confirming that Sr^{2+} does not contribute to charge transport. Activation energy increases, suggesting that Sr^{2+} introduces structural constraints that hinder electron hopping between V^{4+} and V^{5+} ions, reinforcing the small polaron hopping conduction mechanism.

Small Polaron Hopping Mechanism

The values of transition metal ion concentration (N), mean ion spacing (R), and Debye temperature (θ_D) were estimated and found to match with similar values of different transition metal ion borate glasses reported in the literature. Finally, the results further confirmed that charge transport in these glasses obeys a small polaron hopping process between multivalent vanadium ions ($\text{V}^{4+}/\text{V}^{5+}$) and validated that both the mean distance (R) and the activation energy (W) increase with the SrO concentration [23, 24].

Structural Modifications

This decrease in conductivity is associated with the SrO incorporation which drives BO_3 units to turn into BO_4 units. As a result of this transformation the glass network becomes more compact, rigid and contains non-bridging oxygens (NBOs). Therefore, the structural modifications decrease polaron hopping, and hence the conductivity [25].

Conclusion

The effect of strontium oxide (SrO) doping on DC electrical conduction of vanadium borate glasses is systematically analysed in current study. The findings of the study are as follows: The presence of SrO in the vanadium borate glass matrix also led to a decrease of the density, molar volume and oxygen packing density. These changes imply that SrO changes the glass network by imposing the content of non bridging oxygen atoms, leading to the glass increase of structural rigidity and the conduction

pathways. Significant decrease in DC electrical conductivity was found with increase in SrO content. Undoped glass (0 mol% SrO) gave the highest conductivity, and successive additions of SrO result in progressive reduction. The trend of this data suggests that the presence of SrO does not improve ionic or electronic conduction, as SrO is an insulator in the glass framework.

Electrical conduction: The activation energy for electrical conduction increased with higher SrO concentrations and this suggested energy barriers were introduced by the dopant, which hinders electron transport. This implies that the SrO affects the charge carrier mobility through changes in the local glass structure. Mott's small polaron hopping model was used to analyze the conduction mechanism and the results confirm that these glasses mainly carry current electronically by electron hopping between the V^{4+} and V^{5+} states, and not by ionic conduction from the Sr^{2+} ions. The reduced conductivity with SrO doping agrees with this idea that SrO doping disrupts vanadium oxide conduction network. This study generally offers significant insights into the relationship between the composition and the property of strontium doped vanadium borate glasses. Such results may find use in materials optimization for optoelectronic applications where the electrical properties need to be controlled. Further research could also investigate different dopants or modifications of composition in these glasses to improve their conductivity and use this in future technological applications.

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