DIELECTRIC RELAXATION AND IMPEDANCE SPECTROSCOPY OF NASICON TYPE $Na_{3+x}Zr_{2-x}M_xSi_2PO_{12}$ (M = DIVALENT, TRIVALENT, TETRAVALENT ELEMENTS) OXIDES AND ION-IRRADIATION EFFECTS

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(2019 PHZ 8034)

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Dielectric relaxation and impedance spectroscopy of NASICON type $Na_{3+x}Zr_{2-x}M_xSi_2PO_{12}$ (M = divalent, trivalent, tetravalent elements) oxides and ion-irradiation effects

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Dedicated to

My parents and my family for their love, care, and affection

DECLARATION BY THE CANDIDATE

I, **Ramcharan Meena**, hereby declare that the thesis entitled ***" Dielectric relaxation and impedance spectroscopy of NASICON type*** $Na_{3+x}Zr_{2-x}M_xSi_2PO_{12}$ ***(*** M ***= divalent, trivalent, tetravalent elements) oxides and ion-irradiation effects"*** is my original work conducted under the supervision of Prof. Rajendra S. Dhaka and has been approved by the Student Research Committee (SRC) at the Department of Physics, Indian Institute of Technology Delhi, New Delhi, India. Furthermore, I confirm that this work has not been submitted and will not be submitted to any other institute or university for any degree or diploma. I assure compliance with the ethical code of conduct prescribed by the institute. I have duly acknowledged and credited all materials, theoretical analysis, data, figures, and text taken from other sources by appropriately citing them in the thesis. Further, I confirm that I have not used any artificial intelligence (AI) based software for writing any part of the thesis.

Signature _____

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CERTIFICATE OF THE SUPERVISOR

This is to certify that **Ramcharan Meena's** thesis, ***" Dielectric relaxation and impedance spectroscopy of NASICON type*** $Na_{3+x}Zr_{2-x}M_xSi_2PO_{12}$ ***(*** M ***= divalent, trivalent, tetravalent elements) oxides and ion-irradiation effects,"*** submitted to the Department of Physics, Indian Institute of Technology Delhi, for the award of the degree of **Doctor of Philosophy** in Physics, is an original record of his research work. He worked under my supervision and guidance to complete the requirements for submitting this thesis, which I feel reached an acceptable standard. He fulfilled the requirements for submitting the thesis, which, to the best of my knowledge, was of sufficient quality. The thesis results have not been submitted, in part or entirely, to any other university or institute for the award of any degree or diploma.

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Ramcharan Meena

ABSTRACT

In the present era of rapidly growing technology, understanding of various physical properties of materials determines the suitable candidates for various technological applications such as gas sensors, energy storage, memory applications, solar cells, superconductivity, and ionic conductors. $Na_3Zr_2Si_2PO_{12}$ is one of the important members of NASICON (**Sodium S**uper **I**onic **Con**ductors) family has the chemical composition of $Na_{1+x}Zr_2Si_xP_{3-x}O_{12}$, $(0 \leq x \leq 3)$. It shows the structural phase transition from monoclinic to rhombohedral phase at 160°. It shows the wide range of applications in microwave absorption, Na^+-ion batteries, and gas sensors. Microwave heating is used in food preparation, synthesis of materials, local heating in biological samples, and the medical industry. In microwave heating, the dielectric materials absorb the energy depending on the macroscopic permittivity, which is called dielectric loss, and the dielectric permittivity decides the energy storage. Hence, studying the dielectric properties is important for energy storage. The dielectric materials are characterized by measuring the complex permittivity as a function of frequency for constant temperature and as a function of temperature at constant frequency. The dielectric measurements over a wide range of frequencies provide information about the conduction mechanism, polarization mechanism, charge carrier dynamics, and relaxation behavior. $Na_3Zr_2Si_2PO_{12}$ (x=2) and divalent doped NASICON shows the microwave absorption and high electric permittivity at room temperature. however, these studies are limited to room temperature or microwave regions only. Therefore, my Ph.D. thesis is focused on the temperature-dependent dielectric properties of pristine and doped NASICON ceramics. The outlines of the work carried out during this journey are briefly summarized below:

First, the broad area of NASICON materials was introduced. A detailed literature survey on crystal structure, ordering, doping, and synthesis methods is discussed. The applications of NASICON in various fields are discussed. The ion-solid interaction was discussed, and the mechanism of nuclear and electronic energy loss was discussed in detail. Finally, the motivation and objective of the thesis are discussed. In the next part, the sample preparation method, various experimental techniques, and their basic principle were discussed in detail. These techniques are used for different characterizations and analyses in our study. The Rietveld analysis and the steps involved during the analysis were discussed. The working principles of scanning electron microscope (SEM) and transmission electron microscope (TEM) are discussed. The ion irradiation using swift heavy ions (SHI) is described. Various types of electrical transport measurements, such as d.c. resistivity, capacitance-loss measurements, and impedance-phase angle measurements were explained in detail. To proceed further, $Na_3Zr_2Si_2PO_{12}$ bulk samples were prepared to find out the temperature-dependent dielectric properties of pristine NASICON ceramics. The temperature dependence of electric permittivity shows the permittivity of the

order 10^4 at 400 K. The relaxation loss peaks found for low temperatures show thermally activated relaxation. The a.c conductivity follows the universal power law, showing the change in the conduction mechanism at 360 K.

Considering the doping effects on dielectric and impedance properties, we have started with the divalent ion. Ni^{2+} ion are doped into $Na_3Zr_2Si_2PO_{12}$ at the Zr site to improve its dielectric properties. The analysis shows a similar magnitude for electric permittivity up to x=0.15. The relaxation analysis shows a similar type of relaxation for all doped samples. The impedance analysis shows the grain and grain boundary relaxation following the thermally activated relaxation as confirmed by a.c. conductivity analysis. The modulus analysis confirms a similar type of relaxation independent of temperature. In the next part of doping, trivalent (Pr^{3+}) ions are doped at the Zr site in $Na_3Zr_2Si_2PO_{12}$ bulk samples. The larger ionic radii of Pr ions show structural distortions with increasing doping. The permittivity increases by an order of magnitude for all doped samples, showing double relaxation peaks with different activation energies. The Nyquist analysis shows the obtained ionic conductivity of the order 10^{-4} S/cm. The temperature dependence of ac conductivity and related conduction mechanism were investigated using modified power law. In the last part of doping isovalent (Ti) substitutional effects on physical properties of $Na_3Zr_2Si_2PO_{12}$ were studied. The temperature-dependent conductivity measurements show the indication of structural phase transformation. The electric permittivity increases with doping reaches of the order10^7 for 420K. The relaxation mechanism was determined using the non-Debye relaxation models. The impedance analysis is performed using the Z-CPE model. Conductivity analysis using modified power law was performed to determine the conduction mechanism, shows the transformation of the conduction mechanism around 350 K.

The radiation stability of NASICON ceramic was checked using the Au, Ag (100 MeV), and O (90 MeV) irradiation in the fluence range of 5E11 to 5E13 ions/cm^2. The irradiated samples characterization using XRD measurements shows the amorphized type nature heavy ions such as (Au and Ag), while no structural effects were found for O irradiations. Similar types of results were obtained using microscopic TEM analyses. The obtained experimental results were explained using the dominating electronic energy loss mechanism. The last chapter discusses a brief conclusion of this thesis and the possibility of future scopes in this area.

Overall, a systematic investigation of pristine ($Na_3Zr_2Si_2PO_{12}$) and divalent (Ni^{2+}), trivalent (Pr^{3+}) and isovalent (Ti^{4+}) investigations were performed. The radiation stability of NASICON ceramics was checked using swift heavy ions. These studies are useful for finding a suitable candidate for solid oxide fuel cells, charge storage, memory devices, and gas sensors.

सारांश

तेजी से बढ़ती प्रौद्योगिकी के वर्तमान युग में, पदार्थ के विभिन्न भौतिक गुणों की समझ विभिन्न तकनीकी अनुप्रयोगों जैसे गैस संवेदक, ऊर्जा भंडार, स्मृति भंडार उपकरण, सौर सेल, अतिचालकता और आयनिक चालक के लिए उपयुक्त उम्मीदवारों को निर्धारित करती है। $Na_3Zr_2Si_2PO_{12}$ (नासिकॉन) सोडियम आधारित आयनिक अति चालक परिवार के महत्वपूर्ण सदस्यों में से एक है, जिसकी रासायनिक संरचना $Na_{1+x}Zr_2Si_xP_{3-x}O_{12}$,$(0 \leq x \leq 3)$ है। यह 160 ºC पर एकनताक्ष से त्रिसमनताक्ष संरचनात्मक अवस्था में परिवर्तन को दर्शाता है। यह सूक्ष्मतरंग अवशोषण, Na^+-आयन बैटरी और गैस संवेदक में अनुप्रयोगों की विस्तृत श्रृंखला को दर्शाता है। सूक्ष्मतरंग तापन का उपयोग भोजन तैयार करने, सामग्रियों के संश्लेषण, जैविक नमूनों और चिकित्सा उद्योग में किया जाता है। सूक्ष्मतरंग तापन में, परावैद्युत पदार्थ पारगम्यता के काल्पनिक भाग के आधार पर ऊर्जा को अवशोषित करते हैं, जिसे परावैद्युत हानि कहा जाता है, और पारगम्यता का वास्तविक भाग ऊर्जा भंडारण का निर्णय करती है। इसलिए, ऊर्जा भंडारण के लिए परावैद्युत गुणों का अध्ययन महत्वपूर्ण है। परावैद्युत पदार्थों की विशेषता सम्मिश्र पारगम्यता को स्थिर तापमान के लिए आवृत्ति के फलन के रूप में तथा स्थिर आवृत्ति पर तापमान के फलन के रूप में मापकर निर्धारित की जाती है। आवृत्तियों की एक विस्तृत श्रृंखला पर परावैद्युत माप चालन तंत्र, ध्रुवीकरण तंत्र, आवेश वाहक गतिशीलता और विश्रांति के बारे में जानकारी प्रदान करते हैं। $Na_3Zr_2Si_2PO_{12}$ (x=2) और द्विसंयोजी मिश्रित नासिकॉन कमरे के तापमान पर सूक्ष्मतरंग अवशोषण और उच्च विद्युत पारगम्यता दर्शाता है, हालाँकि, ये अध्ययन केवल कमरे के तापमान या सूक्ष्मतरंग क्षेत्रों तक ही सीमित हैं, इसलिए, मेरा शोध प्रबंध असली और मिश्रित नासिकॉन सिरैमिक्स के तापमान पर निर्भर परावैद्युत गुणों पर केंद्रित है। इस दौरान किए गए कार्यों की रूपरेखा संक्षेप में नीचे दी गई है:

सर्वप्रथम नासिकॉन पदार्थ के व्यापक क्षेत्र को पेश किया गया है। क्रिस्टल संरचना, क्रमीकरण, मिश्रित और संश्लेषण विधियों पर विस्तृत साहित्य सर्वेक्षण के साथ विभिन्न क्षेत्रों में नासिकॉन के अनुप्रयोगों पर चर्चा की गई है। आयन–ठोस पारस्परिक प्रभाव पर तथा नाभिकीय और इलेक्ट्रॉनिक ऊर्जा हानि के तंत्र पर विस्तार से चर्चा की गई है। अंत में, थीसिस की प्रेरणा और उद्देश्य पर चर्चा की गई है। अगले भाग में नमूना तैयार करने की विधि, विभिन्न प्रयोगात्मक तकनीकों और उनके मूल सिद्धांतों पर विस्तार से चर्चा की गई है। हमारे अध्ययन में विभिन्न लक्षण–वर्णन और विश्लेषण के लिए इन तकनीकों का उपयोग किया गया है। रीटवेल्ड विश्लेषण और विश्लेषण के दौरान शामिल चरणों पर चर्चा की गई है। सूक्ष्म दर्शन इलेक्ट्रॉन सूक्ष्मदर्शी (एसईएम) और पारदर्शी संचरण इलेक्ट्रॉन सूक्ष्मदर्शी (टीईएम) के कार्य सिद्धांतों पर चर्चा की गई है। तीव्र भारी आयनों (एसएचआई) का उपयोग करके आयन किरणन का वर्णन किया गया है। विभिन्न प्रकार के विद्युत परिवहन माप, जैसे डी.सी. प्रतिरोधकता, धारिता–परावैद्युत हानि तथा प्रतिबाधा–कला कोण माप को विस्तार से समझाया गया है। इसके बाद नासिकॉन सिरेमिक के तापमान पर निर्भर परावैद्युत गुणों का पता लगाने के लिए के थोक नमूने तैयार किए गए। विद्युत पारगम्यता की तापमान निर्भरता 400 K पर 10^4 क्रम की पारगम्यता दर्शाती है। निम्न तापमानों पर पाए गए परावैद्युत हानि प्रभाव, ऊष्मीय रूप से सक्रिय

विश्रांति को दर्शाते हैं। प्रत्यावर्ती धारा चालकता सार्वभौमिक शक्ति नियम का अनुसरण करती है, जो 360 K पर चालन तंत्र में परिवर्तन दर्शाती है।

परावैद्युत और प्रतिबाधा गुणों पर मिश्रिण प्रभाव का अध्ययन के लिए, हमने द्विसंयोजी आयन से शुरुआत की है। इसके परावैद्युत गुणों में सुधार करने के लिए Ni^{2+} आयन को Zr स्थल पर नासिकॉन में अपमिश्रित किया गया है। विश्लेषण से पता चलता है कि x=0.15 तक विद्युत पारगम्यता के लिए समान परिमाण है। विश्राम विश्लेषण सभी मिश्रित किये गए नमूनों के लिए एक समान प्रकार का विश्रांति दर्शाता है। प्रतिबाधा विश्लेषण, तापीय रूप से सक्रिय कण और कण सीमा शिथिलन को दर्शाता है, जैसा कि प्रत्यावर्ती धारा चालकता विश्लेषण द्वारा पुष्टि की गई है। मापांक विश्लेषण तापमान से स्वतंत्र एक समान प्रकार की विश्राम अवस्था की पुष्टि करता है। मिश्रिण के अगले भाग में, त्रिसंयोजक (Pr^{3+}) आयनों को नासिकॉन में Zr स्थल पर अपमिश्रित किया गया है। Pr आयनों की बड़ी आयनिक त्रिज्या बढ़ती डोपिंग के साथ संरचनात्मक विकृतियाँ दिखाती है। सभी मिश्रित किए गए नमूनों के लिए विद्युतशीलता (पारगम्यता) एक परिमाण के क्रम से बढ़ जाती है, जो विभिन्न सक्रियण ऊर्जाओं के साथ दोहरे विश्राम शिखरों को दर्शाती है। नाइक्विस्ट विश्लेषण से 10^{-4} सीमेंस./सेमी के क्रम की आयनिक चालकता प्राप्त होती है। संशोधित शक्ति कानून का उपयोग करके एसी चालकता और संबंधित चालन तंत्र की तापमान निर्भरता की जांच की गई। मिश्रिण के अंतिम भाग में नासिकॉन के भौतिक गुणों पर समसंयोजी (Ti) प्रतिस्थापन प्रभावों का अध्ययन किया गया। तापमान पर निर्भर चालकता माप संरचनात्मक परिवर्तन का संकेत देते हैं। मिश्रिण के साथ विद्युत विद्युतशीलता (पारगम्यता) 420 K पर 10^7 क्रम के परिमाण में जाती है। विश्रांति प्रकार का निर्धारण गैर–डेबाई विश्रांति मॉडल का उपयोग करके किया गया। प्रतिबाधा विश्लेषण प्रतिबाधा-स्थिर चरण तत्व मॉडल का उपयोग करके किया जाता है। चालन तंत्र निर्धारित करने के लिए संशोधित शक्ति कानून का उपयोग करके चालकता विश्लेषण किया गया, जो 350 K के आसपास चालन तंत्र के परिवर्तन को दर्शाता है।

नासिकॉन सिरेमिक की विकिरण स्थिरता की जाँच 5E11 से 5E13 आयन/सेमी^{2} की प्रवाह सीमा में Au, Ag (100 MeV) और O (90 MeV) विकिरण का उपयोग करके की गई। एक्स–रे विवर्तन माप का उपयोग करके विकिरणित नमूनों के लक्षण वर्णन में भारी आयनों जैसे (Au और Ag) के लिए अव्यवस्थित संरचना, जबकि O विकिरणों के लिए कोई संरचनात्मक प्रभाव नहीं पाया गया। पारदर्शी संचरण इलेक्ट्रॉन सूक्ष्मदर्शी (टीईएम)विश्लेषण का उपयोग करके इसी प्रकार के परिणाम प्राप्त किये गये। प्राप्त प्रयोगात्मक परिणामों को प्रमुख इलेक्ट्रॉनिक ऊर्जा हानि तंत्र का उपयोग करके समझाया गया है। अंतिम अध्याय में इस थीसिस का संक्षिप्त निष्कर्ष तथा इस क्षेत्र में भविष्य की संभावनाओं पर चर्चा की गई है।

कुल मिलाकर, मुल नासिकॉन और द्विसंयोजी (Ni^{2+}), त्रिसंयोजी (Pr^{3+}) और समसंयोजी (Ti^{4+}) मिश्रित नासिकॉन का एक व्यवस्थित अध्ययन किया गया है। तेज भारी आयनों का उपयोग करके नासिकॉन सिरेमिक की विकिरण स्थिरता की जाँच की गई। ये अध्ययन आवेश भंडारण, ठोस ऑक्साइड ईंधन सेल, स्मृति भंडारण, गैस संवेदक और विकिरण वातावरण के लिए उपयोगी हैं।

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