

**INFLUENCE OF GRAIN SIZE AND ENVIRONMENTAL
TEMPERATURE ON ION ENERGY LOSS IN MATERIALS:
A COMPREHENSIVE STUDY OF GADOLINIUM-DOPED
CERIA**

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INDIAN INSTITUTE OF TECHNOLOGY DELHI**

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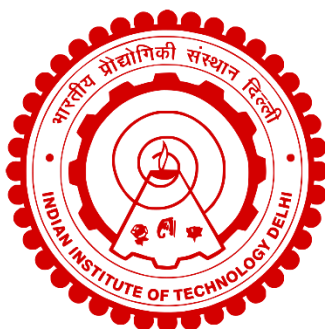
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TEMPERATURE ON ION ENERGY LOSS IN MATERIALS:
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by

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Submitted

in fulfillment of the requirements of the degree of Doctor of Philosophy
to the



INDIAN INSTITUTE OF TECHNOLOGY DELHI
JULY 2025

Dedicated to...

My Parents & Community

DECLARATION BY THE CANDIDATE

I, **Waseem Ul Haq**, declare that the work in this thesis entitled “**Influence of Grain Size and Environmental Temperature on Ion Energy Loss in Materials: A Comprehensive Study of Gadolinium-Doped Ceria**”, is my own work conducted under the supervision of Prof. Santana Ghosh and Prof. Vinita Grover Gupta and approved by student research committee (SRC) at Department of Physics, Indian Institute of Technology Delhi, New Delhi, India. I further declare that this work is not submitted and will not be submitted to any other institute/university for any degree or diploma. I confirm to the norms and guidelines given in the ethical code of conduct of the institute. Moreover, I have given appropriate credit to all materials, theoretical analysis, data, figures, and text used from other sources, by citing them in the text of the thesis.

Signature _____

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CERTIFICATE

This is to certify that the thesis entitled, “Influence of Grain Size and Environmental Temperature on Ion Energy Loss in Materials: A Comprehensive Study of Gadolinium-Doped Ceria”, being submitted by Mr. Waseem Ul Haq to the Indian Institute of Technology Delhi for the award of the degree of ‘Doctor of Philosophy’ is a record of bonafide research work carried out by him under our supervision and guidance. He has fulfilled the requirements for submission of the thesis, which to the best of our knowledge has reached the requisite standard.

The material contained in the thesis has not been submitted in part or in full to any other University or Institute for the award of any degree or diploma.

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Abstract

In the face of ever-increasing demand for nuclear energy, the hunt for materials that can endure the extreme radiation environments of the nuclear industry has become a vital challenge. Ion beam irradiation offers sub-nanometer precision for localized material modification and is applicable across a range of industries. This rapidly advancing field explores ion-induced changes to solids, thin films, surfaces, and interfaces. Moreover, ion beam irradiation, with energy levels ranging from a few electron volts (eV) to giga-electron volts (GeV), is esteemed for its capability to effectively modify the properties of solids at shallow depths.

In a nuclear reactor environment, the interaction of ion beams results in energy loss influenced by the energy of the incoming ions and the material's properties. The two main types of energy loss are nuclear energy loss (S_n) and electronic energy loss (S_e). Radiation resistance to swift heavy ions (SHI) and low-energy heavy ions in order to determine how well they can withstand nuclear fission and alpha recoils, respectively; which can cause significant damage in materials when used as nuclear fuels or waste immobilization matrices. Nuclear energy loss occurs when ions transfer energy (< 100 keV) to atomic nuclei, causing displacement and initiating elastic collisions. This can lead to effects like volume swelling, defect annealing, defect clustering, and strain. In contrast, electronic energy loss (dominates at higher energies) involves ions dissipating energy through ionization, creating a latent track just a few nanometers in size.

In contemporary, materials in the nano-regime are being extensively studied because of significant changes in their optical, electrical, thermal, and mechanical properties. As we reduce particle size, the increase in the surface-to-volume ratio unlocks remarkable enhancements in material properties. It is quite obvious that nano-grain size materials have a significantly larger fraction of grain boundaries compared to their bulk counterparts. It is also speculated that nano-crystalline materials exhibit better radiation tolerance. Grain boundaries can act as "sinks" for defects, absorbing irradiation-induced defects like interstitials and vacancies, which helps reduce their accumulation and minimizes radiation damage. Advanced computational simulations have provided insights into the interactions between grain boundaries (GBs) and irradiation-induced defects, illustrating that these interactions play a crucial role in mitigating the net concentration of defects and, therefore, the overall radiation damage. This is achieved through a mechanism often described as 'loading-unloading.'

Nuclear energy is the leading non-renewable source for electricity generation, known for its high efficiency, abundant uranium availability, and lack of carbon emissions during operation. This makes it a promising alternative, helping to meet global energy demands while reducing air pollution from fossil fuels. The demand for nuclear energy has risen significantly due to the need

for clean and efficient energy sources, especially amid dwindling fossil fuel reserves and climate change challenges. In the future, coal, oil, and natural gas—major pollutants—may be largely replaced by nuclear energy. However, the utilization of uranium as a fuel source in nuclear reactors inevitably generates by-products, primarily plutonium (Pu) and minor actinides (MAs), as a result of the fission process. A possible compelling solution to the challenges posed by surplus plutonium (Pu) and other nuclear waste is to utilize it as fuel in power reactors, specifically through the innovative concept of **Inert Matrix Fuel (IMF)**. IMF must (i) exhibit strong resistance to radiation damage, good compatibility with the *fissile* products, high melting point, high thermal conductivity, ensure good chemical stability and should be transparent to neutrons.

Ceria (CeO_2) is regarded as a surrogate for actinide dioxides with a cubic fluorite-like structure, such as PuO_2 and UO_2 , therefore making it an important surrogate material for studying nuclear materials. It is also well reported that ceria is a promising inert matrix due to isostructural properties with Uranium oxide. Gd_2O_3 , which is a well-known burnable poison used in nuclear reactors, possesses a cubic bixbyite (C-type, Ia-3) structure and is a superstructure of fluorite with 25% oxygen vacancies. Incorporating Gadolinium (Gd^{3+}) into CeO_2 enables the replication of the behavior and performance characteristics of Gd-UO_2 , facilitating comprehensive studies and assessments without direct involvement with uranium-based fuel. This surrogate system enhances experimental safety and provides a valuable platform for investigating reactor dynamics, fuel behavior, and safety protocols, thus contributing to advancements in nuclear technology.

The research in this thesis highlights the necessity for a more comprehensive understanding of how high irradiation temperatures can affect the radiation tolerance of Gd-doped ceria (nano as well as bulk) exposed to swift heavy ions and low-energy ion beam irradiation. The primary goal of this thesis is to meticulously explore and elucidate how environmental temperature and the grain size of a specific material (5 mol% Gd-doped Ceria *i.e.* $\text{Ce}_{1-x}\text{Gd}_x\text{O}_{2-x/2}$ where $x = 0.05$) influence its radiation tolerance. Firstly, we investigated the significant impact of grain size (nano vs bulk) on the radiation tolerance of Gd-doped ceria when exposed to swift heavy ion beam irradiation with 80 MeV Ag ions, simulating the fission fragment process. Secondly, we performed an in-depth analysis of Gd-doped ceria under high-energy ion beam irradiation at elevated temperatures, contributing valuable insights to explore the effect of a nuclear reactor environment. Thereafter, we the critical dependency of electronic energy loss on variations in grain size in Gd-doped ceria, enhancing our understanding of material behavior against 80 MeV Ag and 120 MeV Au ions. Lastly we analyzed the effects of low-energy ion beam irradiation 400n keV Kr and the resultant grain size dependency in Gd-doped ceria, simulating the α -recoil process.

परमाणु ऊर्जा की लगातार बढ़ती मांग के सामने, परमाणु उद्योग के अत्यधिक विकिरण वातावरण को सहन करने वाली द्रव्य की तलाश एक महत्वपूर्ण चुनौती बन गई है। आयन बीम विकिरण स्थानीय द्रव्य संशोधन के लिए उप-नैनोमीटर परिशुद्धता प्रदान करता है और कई उद्योगों में लागू होता है। यह तेजी से आगे बढ़ने वाला क्षेत्र ठोस पदार्थों, पतली फिल्मों, सतहों और अंतरापृष्ठ में आयन-प्रेरित परिवर्तनों का पता लगाता है। इसके अलावा, कुछ इलेक्ट्रॉन वोल्ट (eV) से लेकर गीगा-इलेक्ट्रॉन वोल्ट (GeV) तक के ऊर्जा स्तर के साथ आयन बीम विकिरण को उथली गहराई पर ठोस पदार्थों के गुणों को प्रभावी ढंग से संशोधित करने की क्षमता के लिए सम्मानित किया जाता है।

परमाणु रिएक्टर वातावरण में, आयन बीम की परस्पर क्रिया के परिणामस्वरूप आने वाले आयनों की ऊर्जा और सामग्री के गुणों से प्रभावित ऊर्जा हानि होती है। ऊर्जा हानि के दो मुख्य प्रकार परमाणु ऊर्जा हानि और इलेक्ट्रॉनिक ऊर्जा हानि हैं। तीव्र भारी आयनों और कम ऊर्जा वाले भारी आयनों के लिए विकिरण प्रतिरोध, यह निर्धारित करने के लिए कि वे क्रमशः परमाणु विखंडन और अल्फा रिकॉइल्स का कितना अच्छा सामना कर सकते हैं; जो परमाणु ईंधन या अपशिष्ट स्थिरीकरण मैट्रिक्स के रूप में उपयोग किए जाने पर सामग्रियों में महत्वपूर्ण क्षति का कारण बन सकता है। परमाणु ऊर्जा हानि तब होती है जब आयन परमाणु नाभिक में ऊर्जा (<100 keV) स्थानांतरित करते हैं, जिससे विस्थापन होता है और लोचदार टकराव शुरू होता है। इससे आयतन सूजन, दोष एनीलिंग, दोष क्लस्टरिंग और तनाव जैसे प्रभाव हो सकते हैं। इसके विपरीत, इलेक्ट्रॉनिक ऊर्जा हानि (उच्च ऊर्जा पर हावी) में आयनीकरण के माध्यम से ऊर्जा को नष्ट करना शामिल होता है, जिससे केवल कुछ नैनोमीटर आकार का एक अव्यक्त मार्ग बनता है।

समकालीन समय में, नैनो-शासन में सामग्रियों का उनके प्रकाशिकी, विद्युतीय, तापीय और यांत्रिक गुणों में महत्वपूर्ण परिवर्तनों के कारण बड़े पैमाने पर अध्ययन किया जा रहा है। जैसे-जैसे हम कण आकार को कम करते हैं, सतह-से-आयतन अनुपात में वृद्धि से भौतिक गुणों में उल्लेखनीय वृद्धि होती है। यह बिल्कुल स्पष्ट है कि नैनो-ग्रेन आकार के द्रव्यों में उनके थोक समकक्षों की तुलना में ग्रेन

की सीमाओं का काफी बड़ा हिस्सा होता है। यह भी अनुमान लगाया गया है कि नैनो-क्रिस्टलीय सामग्री बेहतर विकिरण सहनशीलता प्रदर्शित करती है। ग्रेन की सीमाएं दोषों के लिए "सिंक" के रूप में कार्य कर सकती हैं, अंतरालीय और रिक्तियों जैसे विकिरण-प्रेरित दोषों को अवशोषित करती हैं, जो उनके संचय को कम करने में मदद करती हैं और विकिरण क्षति को कम करती हैं। उन्नत संगणकीय अनुकरण ने ग्रेन सीमाओं और विकिरण-प्रेरित दोषों के बीच अंतर्क्रिया में अंतर्दृष्टि प्रदान की है, जिससे पता चलता है कि ये अंतर्क्रिया दोषों की शुद्ध एकाग्रता को कम करने में महत्वपूर्ण भूमिका निभाते हैं और इसलिए, समग्र विकिरण क्षति होती है। यह एक तंत्र के माध्यम से प्राप्त किया जाता है जिसे अक्सर 'लोडिंग-अनलोडिंग' के रूप में वर्णित किया जाता है।

परमाणु ऊर्जा बिजली उत्पादन के लिए प्रमुख गैर-नवीकरणीय स्रोत है, जो अपनी उच्च दक्षता, प्रचुर यूरेनियम उपलब्धता और संचालन के दौरान कार्बन उत्सर्जन की कमी के लिए जाना जाता है। यह इसे एक आशाजनक विकल्प बनाता है, जो जीवाश्म ईंधन से वायु प्रदूषण को कम करते हुए वैश्विक ऊर्जा मांगों को पूरा करने में मदद करता है। स्वच्छ और कुशल ऊर्जा स्रोतों की आवश्यकता के कारण, विशेष रूप से घटते जीवाश्म ईंधन भंडार और जलवायु परिवर्तन की चुनौतियों के बीच, परमाणु ऊर्जा की मांग काफी बढ़ गई है। भविष्य में, कोयला, तेल और प्राकृतिक गैस - प्रमुख प्रदूषक - को बड़े पैमाने पर परमाणु ऊर्जा द्वारा प्रतिस्थापित किया जा सकता है। हालाँकि, परमाणु रिएक्टरों में ईंधन स्रोत के रूप में यूरेनियम का उपयोग अनिवार्य रूप से विखंडन प्रक्रिया के परिणामस्वरूप उप-उत्पाद, मुख्य रूप से प्लूटोनियम (Pu) और माइनर एक्टिनाइड्स उत्पन्न करता है। अधिशेष प्लूटोनियम (Pu) और अन्य परमाणु कचरे से उत्पन्न चुनौतियों का एक संभावित सम्मोहक समाधान इसे बिजली रिएक्टरों में ईंधन के रूप में उपयोग करना है, विशेष रूप से इनर्ट मैट्रिक्स ईंधन की अभिनव अवधारणा के माध्यम से। इनर्ट मैट्रिक्स ईंधन को (i) विकिरण क्षति के प्रति मजबूत प्रतिरोध, विखंडनीय उत्पादों के साथ अच्छी अनुकूलता, उच्च गलनांक, उच्च तापीय चालकता, अच्छी रासायनिक स्थिरता सुनिश्चित करनी चाहिए और न्यूट्रॉन के लिए पारदर्शी होना चाहिए।

सेरिया (CeO_2) को क्यूबिक फ्लोराइट जैसी संरचना वाले एक्टिनाइड डाइऑक्साइड, जैसे कि PuO_2 और UO_2 , के लिए एक सरोगेट माना जाता है, इसलिए यह परमाणु द्रव्य के अध्ययन के लिए एक महत्वपूर्ण प्रत्यौषधि सामग्री बन जाता है। यह भी अच्छी तरह से बताया गया है कि यूरेनियम ऑक्साइड के साथ आइसोस्ट्रक्चरल गुणों के कारण सेरिया एक आशाजनक निष्क्रिय मैट्रिक्स है। Gd_2O_3 , जो परमाणु रिएक्टरों में इस्तेमाल किया जाने वाला एक प्रसिद्ध जलने योग्य जहर है, इसमें क्यूबिक बक्सबाइट (C- Type, Ia-3) संरचना होती है और यह 25% ऑक्सीजन रिक्तियों के साथ

फ्लोराइट की एक अधिरचना है। गैडोलीनियम को Gd^{3+} में CeO_2 में शामिल करने से $Gd-UO_2$ के व्यवहार और प्रदर्शन विशेषताओं की प्रतिकृति सक्षम हो जाती है, जिससे यूरेनियम-आधारित ईंधन के साथ सीधे जुड़ाव के बिना व्यापक अध्ययन और मूल्यांकन की सुविधा मिलती है। यह सरोगेट प्रणाली प्रायोगिक सुरक्षा को बढ़ाती है और रिएक्टर गतिशीलता, ईंधन व्यवहार और सुरक्षा प्रोटोकॉल की जांच के लिए एक मूल्यवान मंच प्रदान करती है, इस प्रकार परमाणु प्रौद्योगिकीय की प्रगति में योगदान देती है।

इस थीसिस में शोध इस बात की अधिक व्यापक समझ की आवश्यकता पर प्रकाश डालता है कि उच्च विकिरण तापमान तेजी से भारी आयनों और कम-ऊर्जा आयन बीम विकिरण के संपर्क में आने वाले जीडी-डॉप्ड सेरिया (नैनो और साथ ही बल्क) की विकिरण सहनशीलता को कैसे प्रभावित कर सकता है। इस थीसिस का प्राथमिक उद्देश्य सावधानीपूर्वक पता लगाना और स्पष्ट करना है कि पर्यावरणीय तापमान और एक विशिष्ट द्रव्यों के ग्रेन का आकार (5 mol% Gd-doped Ceria यानी $Ce_{1-x} Gd_x O_{2-x/2}$ जहां $x = 0.05$) इसके विकिरण को कैसे प्रभावित करते हैं सहनशीलता। सबसे पहले, हमने विखंडन टुकड़े की प्रक्रिया का अनुकरण करते हुए, 80 MeV Ag आयनों के साथ तेज भारी आयन बीम विकिरण के संपर्क में आने पर Gd-डोपेड सेरिया की विकिरण सहनशीलता पर ग्रेन के आकार (नैनो बनाम थोक) के महत्वपूर्ण प्रभाव की जांच की। दूसरा, हमने ऊंचे तापमान पर उच्च-ऊर्जा आयन बीम विकिरण के तहत जीडी-डॉप्ड सेरिया का गहन विश्लेषण किया, जिससे परमाणु रिएक्टर वातावरण के प्रभाव का पता लगाने के लिए मूल्यवान अंतर्दृष्टि का योगदान हुआ। इसके बाद, हम Gd-डॉप्ड सेरिया में ग्रेन के आकार में भिन्नता पर इलेक्ट्रॉनिक ऊर्जा हानि की महत्वपूर्ण निर्भरता, 80 MeV Ag और 120 MeV Au आयनों के खिलाफ सामग्री व्यवहार की हमारी समझ को बढ़ाते हैं। अंत में हमने α -रीकॉइल प्रक्रिया का अनुकरण करते हुए कम-ऊर्जा आयन बीम विकिरण 400n keV Kr के प्रभावों और Gd-doped सेरिया में परिणामी ग्रेन के आकार की निर्भरता का विश्लेषण किया।

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XPS Spectra of O 1s spectra for 5 mol% Gd-Doped Ceria. a). O 1s spectra of Pristine S800. b). O 1s spectra of S800 irradiated with 400 KeV kr; fluence 1×10^{17} ions/cm². c). O 1s spectra of Pristine S1000. d). O 1s spectra of S1000 irradiated with 400 KeV kr; fluence 1×10^{17} ions/cm². e). O 1s spectra of Pristine S1300. f). O 1s spectra of S1300 irradiated with 400 KeV kr; fluence 1×10^{17} ions/cm².

Figure 6.7

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Ce³⁺/Ce⁴⁺ ratio obtained from XPS.

Figure 6.8

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Schematic showing the particle size variation and defects annealing via grain boundaries. Red clusters encircled in black are mobile clusters as they are located near the grain boundaries. Red clusters encircled in red are immobile clusters as they are located away from the grain boundaries.

Figure 6.9

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Nomenclature

Ag: Silver

Ce: Cerium

FWHM: Full Width at Half Maxima

GBs: Grain Boundaries

Gd: Gadolinium

GDC: Gadolinium doped ceria

GIXRD: Glancing Incidence X-ray Diffraction

g : Electron phonon coupling constant / factor / strength

HT: High Temperature

IMF: Inert Matrix Fuel

K : Lattice thermal conductivity

Kr : Krypton.

MA: Minor Actinides

NC: Nano-crystalline

RT: Room Temperature

FESEM: Field Emission Scanning Electron Microscopy

SHI: Swift Heavy Ions

SEs: Secondary Electrons

S_e : Electronic energy loss

S_n : Nuclear energy loss

TEM: Transmission Electron Microscopy