Preparation of High Entropy Titanite Pyrochlore and Radiation Stability Study

Adam Gootgeld
agootge@g.clemson.edu

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PREPARATION OF HIGH ENTROPY TITANITE PYROCHLORÉ
AND RADIATION STABILITY STUDY

A Thesis
Presented to
the Graduate School of
Clemson University

In Partial Fulfillment
of the Requirements for the Degree
Master of Science
Materials Science and Engineering

by
Adam Michael Gootgeld
August 2023

Accepted by:
Dr. Kyle Brinkman, Committee Chair
Dr. Jianhua Tong
Dr. Dilpuneet Aidhy
ABSTRACT

Pyrochlore has been studied as a host phase for safe storage of radionuclides and exists naturally with long-term stability with good long-range order [1]. High entropy oxides show promising tunable properties that could demonstrate favorable bulk deposit of radioactive materials such as spent nuclear fuel (Uranium and other actinides). It is proposed that using high entropy oxides (HEOs) as the cation in this framework will shift the gibbs free energy so that radioactive nuclear waste will be stabilized for safe, long-term, eco-friendly storage. We have established a consistent method to fabricate high entropy titanite pyrochlores. In this study, ion beam irradiation (600 keV Ar ion) is used to produce displacement damage and simulate alpha decay damage from self-radiation damage in nuclear waste. GIXRD and TEM are used to analyze depth of the damages layer of various irradiation High Entropy Pyrochlore in effort to see if radiation stability properties are increased. In-Situ TEM (1 MeV Kr) is also used to study radiation induced amorphization, revealing a lack of enhanced stability from an increase in cations in pyrochlores A-position. The subsequent research has shown parallels to literature review.
DEDICATION

I would like to dedicate this work to my Grandpa Alan Gootgeld and my late Grandpa Manuel Aguirre. They have been the most inspiring role models in my life. Their ability to see the big picture in life shines beyond any minor problem that distracts us an individuals from seeing the good that humans are created in. Albeit the purpose they bring to the world, their families, their hobbies, and to themselves were continuously perceptible in a way the motivates me to bring the same mindful approach to the issues present around me, in light of charity and good will. I have not mastered the image they have set for me but am always cognizant of what it takes to follow in their footsteps.

I also want to thank my parents Mike and Lori, and my sister Emily for consistently supporting me through my research three to six time zones away.
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I would like to express my sincere gratitude to Dr. Tang, my advisor, for his invaluable guidance. I consider myself fortunate to have found such an exceptional advisor in the field of research that I am passionate about. There is never a time that I feel invalidated by Dr. Tang’s counseling and calm approach to instruction that enables a powerful learning environment for all students. Also, his knowledge in the nuclear field is respected amongst the niche global community which creates an successful working environment.

I would like to thank all my past and present lab members for being with me on this journey and assisting me with this research in one way or another. Matthew Page, Claude De Lamater-Brotherton, Anne Romine, Peyton McGuire, Youyuan Zhang, and Yuying Wen are all great friends I have made from this experience. Each has brought their own strengths to the lab group and have helped in essential ways throughout my research with Dr. Tang’s lab group. Likewise, the Electron Microscopy Lab staff, Dr. Haijun Qian, Dr. Lax Saraf, Dayton Cash, and Donald Mulwee were all very knowledgeable and extremely helpful while I was learning scanning electron microscopy.

I also would like to thank Daniel Thompson from the physics department for help with the Spark Plasma Sintering machine and Colin McMillen for help with Grazing Incidence Diffraction in the chemistry department.
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CHAPTER 1. INTRODUCTION

1.1 Motivation

Nuclear power is the second-largest source of low-carbon electricity today in the world and is the largest source of reliable energy output without the presence of harmful carbon emissions in the United States [8]. Albeit nuclear energy’s environmental impact is low, its development isn’t as quick as it could be due to political and social issues that are present when examining the hazards of nuclear waste and its disposal. Research dedicated to new waste streams and radiation resistance materials can bring a cleaner image to the production and manufacturing of Nuclear Energy.

Hence, the peaceful use of nuclear energy will inevitably require a strategy for the disposal of actinides and particularly fissile $^{239}$Pu and $^{235}$U. In addition to the plutonium and uranium, “minor” actinides such as $^{237}$Np, $^{241}$Am-$^{243}$Am, and $^{244}$Cm are also generated in reactors. Because isotopes such as $^{239}$Pu (half-life = 24,100 a) and $^{237}$Np (half-life = 2,100,000 a) are long lived isotopes, the radiotoxicity of $^{239}$Pu, $^{237}$Np, and their fission products will be a risk over geological time scales ($10^5$–$10^6$ a) [9]. Therefore, various materials have been proposed for the immobilization and dispose of plutonium and various actinides.

In recent years, there has been growing interest in radiation tolerant ceramics, whose potential applications range from nuclear fuel forms, nuclear waste forms, and insulators for fusion reactor diagnostics. When examining host materials specifically, stability can be diagnosed through various disciplines including thermodynamically favorability, chemical durability, and radiation damage stability.

Though numerous criteria can be defined to assess radiation tolerance, resistance to amorphization is widely accepted as a necessary materials design criterion. In application, host materials are self-radiated by the decomposition of fission products in the form of alpha decay. Thus, amorphization resistance is an important attribute as irradiation-induced amorphization transformations are usually accompanied by large and undesirable volume changes, apparent void swelling, and changes in mechanical properties. The
radiation tolerance is found to vary significantly from material to material making radiation damage testing a tool to hypothesis a particular materials reliability to be a potential nuclear waste host.

In some studies waste form development has turned to natural geological and mineralogical investigations of analogous crystalline phases in natural environments[9]–[12]. Pyrochlore, zirconolite, baddeleyite, zircon, or monazite, are all minerals that are well known for their durability, that endure as placer deposits in stream beds after surviving sometimes several cycles of weathering, erosion, transport, and deposition. [9] The underlying concept of mineralogical studies is that they can be employed to gain insight into the long-term performance of the ceramic nuclear waste form under conditions similar to those expected for geological repositories [12]. In particular, pyrochlore structure-type materials are also promising candidates as potential host phases for actinides [13]. Several natural occurring pyrochlore structures have been observed to include actinides [14], and in nature pyrochlores are also common in highly evolved rock types like pegmatites and carbonatites.

To assess the lab synthesized pyrochlore for the potential host phase for fission products, Ion beam radiation has been proven to simulate the self-irradiated alpha decay as a result of decaying fission products and actinides within the phase. Energetic heavy ion-beam irradiation, as a useful tool for simulating neutron-irradiation and for ion implantation, has been widely applied applications ranging from the search and development of radiation resistant materials for fission reactors to searching and developing materials for radioactive waste forms. Furthermore, characterization after Ion beam can report a materials radiation stability and allow researchers modifications to the phase to be explored.

In supposition, ceramic waste forms are custom-made to incorporate waste components as part of their crystal structure based on information from naturally found minerals containing radioactive and non-radioactive species similar to the radionuclides of concern in wastes from fuel reprocessing. The theory is that this tailored phase customized by the waste stream can settle is low free energy states that are demonstrated in nature, for long-term-storage. The ability to create single-phase ceramic mimic naturally occurring crystals substantiates the long-term stability of such crystals over geologic timescales of interest
for nuclear waste immobilization which can be tested via Ion beam irradiation techniques and then characterized to determine phase change or amorphization.

1.2 Background

Amorphization transformations by irradiation frequently involve substantial and unfavorable volume changes, apparent void swelling, and modifications to mechanical characteristics. Consequently, amorphization resistance materials can serve as solutions ranging from nuclear fuel forms to insulators for fusion reactor diagnostics. Because pyrochlore has a structural compatibility with big radionuclide species such as elements in the actinide series, it is projected that it may be resistant to radiation-induced amorphization[15]. It is also proposed that the addition of multiple elements to a single position in a single phase can increase entropy, and in theory contribute to a materials radiation stability.

1.2.1 Pyrochlore

The pyrochlore structure, $A_2B_2O_7$ (referred to as a 2:2:7 compound) is a derivative from the ordered fluorite structure $MX_2$. This cubic structure is composed of two 3+ atoms in the A site, two 4+ atoms in the B site, and 7 oxygens -with an oxygen vacancy, one in every eight interstitial sites seen in Fig. 1. This oxygen vacancy provides interesting properties to give reason to further research with pyrochlore on everything from high temperature thermal barrier coatings, solid oxide fuel cell, ionic/electrical

![Fig. 1.2.1 - Schematic drawing showing crystal structures of ideal pyrochlore ($A_2B_2O_7$)](image)
conductors, and nuclear waste immobilization. One-eighth of the anions are missing, to compensate the reduced charge of the A\(^{3+}\) cations. The eight-coordinated A sites (16c) located within a distorted cubic coordination polyhedron are typically occupied by lanthanides such as La, Nd, Gd, Dy, Ho, or trivalent actinides. The six-coordinate B sites (16d) located within a distorted octahedron are usually occupied by a smaller cation, such as Ti, Zr, Hf, or Sn, [16] but is also postulated to hold UO\(_2\); the theoretical host site for fission products.

The unit cell for the ideal pyrochlore crystal structure is shown in Fig.1. The A-site cation is represented by yellow spheres, the B-site is represented by blue spheres, and oxygen anions are represented in red. One eighth of the oxygen atoms are highlighted in white (Fig. 1), displaying the vacancy that is a defining characteristic of the pyrochlore crystal structure. These oxygen vacancies are ordered on the pyrochlore anion sublattice. This vacant site provides the pyrochlore structure with the remarkable ability to tolerate structural distortions. Moreover, pyrochlore oxides can accommodate variable degrees of cation and/or anion disordering depending on intrinsic (e.g., chemical composition, bonding character, and cations size mismatch, rA/rB) as well as extrinsic factors [17][18][19]. Ideal (ordered) pyrochlore oxides are isometric [space group (SG) =Fd\(\overline{3}\)m (227)] and characterized by the A\(_2\)B\(_2\)O\(_7\) ideal stoichiometry. As discussed, the oxygen-deficiency in the ideal pyrochlore structure creates a vacancy that is easily accessible for anions in defect phases. This cubic crystal, related to the fluorite structure, can accommodate a range of solid solutions between BO\(_2\) and A\(_2\)O\(_3\) compounds which has determined that it is possible to host actinides [19], as well as previously discussed UO\(_2\). Elemental versatility ensures that pyrochlore compounds exhibit a variety of interesting properties.[20]

Pyrochlore can be defined by signature peaks through X-ray diffraction. The appearance of the peak (111) around 2 theta angle 15 degree signifies the ordered pyrochlore, and the strongest peak (222) is close to 30 degrees. These peaks shift depending on the size of the cations and how they fit in the cubic structure. The fit of x-ray diffraction (XRD) data can be a tool to calculate insight on individual sample such as
crystallite or grain size, but more importantly can provide a unit cell parameter “a” that can be used to calculate lattice parameter indicating geometry of the unit cell in a crystal lattice.

![Figure 1.2](image1.png)

**Fig. 1.2.2 - Sm₂Ti₂O₇ X-ray Diffraction pattern (XRD)**

The synthesis of pyrochlore can be achieved through a variety of sintering techniques. Starting materials depicted in the phase diagram above show the A₂O₃ sesquioxide (shown on left side of Fig.2) and the AO₂

![Figure 3](image2.png)

**Fig. 3 - Sm₂O₃ - TiO₂ phase diagrams [1], [2]**
rutile (shown in Fig.3) mixing to create an assortment of phases. Figure 3 shows pyrochlore appearing as a line compound reproduced from 2-1-6 is a 60-40 mixed phase – sesquioxide to rutile respectively – mixed at a temperature above at least 1400 for significant grain growth, but below 1800 to avoid an $\beta$ phases. There are some variances between titanate two-phase diagrams, especially in the region of the pyrochlore phase. Though the qualitative information is useful, inconsistency in the titanate series of phase diagrams is consistent amongst synthesis applications [1], [2]

Several radiation-damage studies have been performed on synthetic pyrochlores. The cubic structure (Fd3m) of pyrochlore ($A_2B_2O_7$) can take on many compositions through charge compensation between the A and B sites ($A(3+)B(4+)O_7$ and $A(2+)B(5+)O_7$, for example) or on the A site alone ($A(2+)_{0.5}A(4+)_{0.5}B(4+)O_7$, for example). In the case of Pu immobilization, the B site is occupied by Ti, principally, and the A sites by Gd, Hf, U(IV), Pu(IV), and Ca [21]. Studies on $^{244}$Cm-substituted pyrochlore have shown that the pyrochlore structure becomes amorphous between $3 \times 10^{18}$ and $4 \times 10^{18}$ $\alpha$ decays/g (hereinafter $\alpha$/g) when Ti occupies the B site [22], [23]and, from ion-beam irradiation studies, greater than $3 \times 10^{20}$ $\alpha$/g when Zr occupies the B site [24].

Swelling is another type of observation that can display the increase of volume and decrease of density of materials subjected to intense radiation. Neutrons impacting the material's lattice rearrange its atoms, causing buildup of dislocations and voids. Pyrochlore structures have been observed to swell between 3% and 10% during the process of becoming amorphous from radiation-induced damage [25]Wald and Offerman (revised in Weber and Ewing [26]) found that the bulk dimensions of a 3 mass% $^{244}$Cm-bearing Gd$_2$Ti$_2$O$_7$ swelled 5.5% when a dose of $3.2 \times 10^{18}$ $\alpha$/g was accumulated.
1.2.2 High Entropy Oxide

Multi-component, high-entropy, or entropy stabilized oxides have high configurational entropy, which makes them possess higher structural stability than their parent counterparts [27]. Disordered elements in single structure phases can lead to higher structural stability, superior corrosion resistance, and enhanced mechanical properties. The compositional complexity of high-entropy ceramics contributes to sluggish diffusion, slow energy dissipation, damage accumulation and defect migration, and thereby resulting in limited recombination of irradiation-induced defects [28]. Moreover, the sluggish diffusion effect of high-entropy ceramics can also lead to smaller grain and higher grain boundary density during the long-time sintering and densification. Irradiation-induced point defects can annihilate harmlessly at grain boundaries, thus reducing the possibility of forming defect clusters and voids. [29]

High entropy ceramics are consisted of five or more principal cations with different mass and ionic radii and therefore will cause severe lattice distortion and sluggish diffusion rate of ions. It has been demonstrated that irradiation resistance, mechanical stability, and corrosion resistance of HE materials can be remarkably enhanced.[30]

\[
S_{\text{Config}} = -R \left[ x \left( \sum_{a=1}^{M} x_a \ln(x_a) \right) \right]_{\text{cation site}}
\]

Eq 1.2.1 Configurational entropy (\(S_{\text{Config}}\)) of single cation sub-lattice (fluorite)

High entropy systems can be reached when all the elements are present in equimolar proportion. In Eq.1, five or more elements in near-equiiatomic proportions are required to achieve (\(S_{\text{Config}}\)) \(\geq 1.5R\). This \(S_{\text{Config}}\) calculation (Eq.1) is only valid for ideal solid solutions, which is rarely the case. Furthermore, this specific equation takes a single cation site into account, such as in rock salt where the mole fraction of each of the elements is 0.2 (resulting in \(S_{\text{Config}} = 1.61R\)) [31]. In HEO’s only the cationic mole
fraction is considered. For instance, in systems like pyrochlore, \((\text{Eu}_{0.2}\text{Gd}_{0.2}\text{Sm}_{0.2}\text{Dy}_{0.2}\text{Ho}_{0.2})_2\text{B}_2\text{O}_7\), the \((S_{\text{Config}})\) calculation is not straightforward as the site occupancies of the cations (due to possible inversion) are often unknown.

\[
S_{\text{Config}} = -R \left[ x \left( \sum_{a=1}^{M} x_a \ln(x_a) \right)_{\text{A-site}} + y \left( \sum_{b=1}^{N} y_a \ln(y_a) \right)_{\text{B-site}} + z \left( \sum_{o=1}^{P} z_a \ln(z_a) \right)_{\text{C-site}} \right]
\]

Eq 1.2. \(x, y, \) and \(z\) being the mole fractions of the elements present in the A-site, B-site and O\(^2\)-site (or anion site), respectively. While \(M, N\) and \(P\) are the number of cations present on A-sites, B-sites and anions on O\(^2\)-sites, respectively.

High Entropy materials recent success has been in alloys. HEA’s have been able to raise the yield strength \(\sigma_y\) while conceding as little ductility as possible and preserving a high \(\epsilon_u\). This is challenging because strength and ductility usually exhibit a trade-off: a gain in \(\sigma_y\) is normally accompanied by a sacrifice in \(\epsilon_u\) [32].

HEAs have become tightly associated with finding single-phase solid solutions by controlling configurational entropy. This causes controversy and distracts from the major objective of exploring the immense number of alloys in the central regions of hyper-dimensional composition space[33]. There are several terms that evoke the vastness of composition space without any implications concerning the magnitude of entropy or the types of phases present. These terms include multi-principal element alloys (MPEAs), complex concentrated alloys (CCAs) and baseless alloys. The hope to create long range order is not concluded in this study but order can also be defined as having a solid solution (SS), thus even elemental distribution is assumed to be absent in High Entropy Materials.
1.2.3 High Entropy Oxide Pyrochlore

An assumed concept of high-entropy materials for the purpose of immobilization of HLW continuous the motivation for potential application of high-entropy $\text{A}_2\text{B}_2\text{O}_7$ ceramics. As discussed, pyrochlore is an important class of structural/functional ceramic and has a wide range of applications, such as solid oxides ion conductors, thermal barrier, and a promising host matrix for the immobilization of minor actinides [15], [34]. Multiple cations can thus be added to the A-site ($3^+$ elements such as rare earth lanthanides) and B sites ($4^+$ elements such as a transition metals or post-transition metals). The larger $A^{3+}$ cation is depicted in yellow, dark blue, pink, green, and orange. All sharing the position of the A-site cation with a coordinated to eight oxygen atoms (two 8b oxygen ions and six 48f oxygen ions). The smaller $B^{4+}$ cation shown in blue is coordinated to six oxygen ions located on the 48f. This position could host a variety of $4^+$ cations such as (Zr, Hf, Ce, Sn, etc.) but is kept to just titanium for the consistency of this experiment. Just as single component pyrochlore, there is still an oxygen vacancy at 8a, which is surrounded by four $B^{4+}$ cations shown in red. It is theoretical possible to extend pyrochlore solid solution to high entropy.

![Schematic drawing showing crystal structures of 5-A component pyrochlore ($A_2B_2O_7$)](Eu0.2Gd0.2Sm0.2Ho0.2Dy0.2)Ti2O7

Fig. 3. Schematic drawing showing crystal structures of 5-A component pyrochlore ($A_2B_2O_7$)
pyrochlore oxides due to the addition of equal ratios of cations on either the A, B, or A and B sites employing the high-entropy design concept. The high entropy pyrochlore oxides may be endowed with higher functional tunability or unexpected physical properties, compared with traditional pyrochlore oxides with one or two cations in the leading position.

HEO became a promising candidate for the A site of the pyrochlore phase, as the was a naturally stable phase in nature and could possibly hold uranium in the B position. It does require lots of mixing and heat to sinter ceramic. Rare-earth-sesquioxide metals in A position fulfills the HEO requirement while containing rare-earth sesquioxides $R_2O_3$ ($Sm_2O_3$, $Eu_2O_3$, $Gd_2O_3$, etc.), which are a part of bixbyite group, exhibit both high chemical durability and solubility for actinides and other radionuclides, so that it is feasible to dope an actinide bearing waste-form or fuel-form with rare-earth to serve as depletable neutron absorbers [35]. Moreover, the B-site could theoretically contain any number of 4+ cations for immobilization of or even this site could host an actinide such as $UO_2$. Therefore, synthesizing a high-entropy pyrochlore structure could be a promising strategy to obtain material with superior irradiation resistance for nuclear waste management, insight for HLW host materials and candidate material for nuclear system shielding. [29]

### 1.3 Interactions Between Energetic Ions and Matter

Interactions between energetic electrons and ions with crystal structures result in defects and imperfections. These defects can, in turn, produce changes in the physical, mechanical, and chemical properties of the material [36], [37]. In order to better understand the concept of radiation damage, the mechanisms of radiation damage caused by these particles and their corresponding effects will be discussed. Due to the scope of this research, we will mainly focus on the mechanisms related to energetic ions and their interactions with the crystalline structure of ceramic materials.
1.3.1 – Penetration of Ions in Matter and the Projected Range of Ions

The total stopping power, or an ion’s energy loss per unit pathlength, comprises energy loss from coulombic interactions of the ion with the atomic nucleus of the target (nuclear stopping power) and with the target’s atomic electrons (electronic stopping power). Stopping power and range data are commonly needed for applications such as radiation therapy, radiation protection, ion implantation, and accelerator physics, as well as in basic sciences such as nuclear and particle physics. [38]

\[
R = \int_{0}^{E_0} S^{-1} dE
\]

Equation 1.3.1 - The general expression for the range of ions in solids. [33]

where \(E_0\) is the initial kinetic energy of the particle, \(R\) is the total distance traveled by the ion such that its final energy is zero, and \(S^{-1}\) is the stopping power. The total stopping power is given by,

\[
S = S_n + S_e
\]

Equation 1.3.2 – Total electron stopping power [33]

where \(S_n\) is the nuclear stopping power and \(S_e\) is the electronic stopping power. The relative importance of these energy loss mechanisms (i.e., electronic, or nuclear) depends mostly on the velocity of the ion. For velocities lower than the velocity of the atomic electrons, nuclear energy loss dominates. For higher projectile velocities, electronic energy loss dominates.

The average pathlength traveled by a beam of ions coming to rest is known as its penetration range [38]. The trajectory of ions in solids is conveniently described as a sequence of straight tracks where electronic energy loss occurs. These are separated by nuclear collisions, where nuclear energy loss and large angular deflection occur. The projected range of an ion refers to the average
of the maximum depth that the incident ions reach in the material. However, since the path of the ions is not a straight line but a “zig-zag” trajectory due to nuclear collisions with the material’s atoms, the total path length is longer than the projected range. In other words, the projected range corresponds to the projection of the total path on an axis perpendicular to the surface as illustrated in Figure 5.

![Diagram](image)

**Figure 1.3.3 -** An ion incident on a semiconductor penetrates with a total path length $R$, which gives a projected range, $R_p$, along the direction parallel to the incident ion. [39]

1.3.2 – The Primary Knock-On Atom

The “primary knock-on atom” (PKA) typically refers to the first atom that is displaced by the incoming high-energy ion, usually at or near the surface of the material. Depending on the energy transfer between the incident ion and the PKA, the PKA can then propagate throughout the structure and in turn create secondary knock-on atoms before stopping (a collision cascade). A molecular dynamic simulation of a collision cascade is illustrated in Figure 6.
This can result in the creation of multiple vacant lattice sites and agglomeration of point defects which are collectively known as a “displacement cascade”. During these collision processes, thermal spikes may also be created by the nuclei entering into higher energy states at their lattice position. The idea of a “displacement cascade” then led to the creation of a displacement spike model. The model consists of the creation of several vacant sites, commonly referred to as depleted zones, surrounded by a higher number of interstitials.

1.3.3 – Displacement per Atom

A useful and widespread measure of radiation damage is the “displacements per atom” (DPA). DPA corresponds to the total number of atoms displaced from their original position due to interactions between incident ions and the target atoms and between the PKA and the target atoms. The DPA is calculated as the number of vacancies created, in addition to replacement collisions. A replacement collision occurs when the incident ion knocks a target atom out of its structure position. This target atom will then undergo more nuclear collisions with target atoms, until it transfers the remainder of its energy to knock out a similar target atom. Then, it can replace the target atom it knocked out, resulting in a correct arrangement in the structure but a change from
DPA serves as a unit of measurement for radiation damage and is affected by the material’s atomic density, structure, and ion fluence. A general expression for the calculation of DPA is given by,

\[
dpa = \frac{\phi N_d}{\rho}
\]

Equation 1.3.5 – DPA calculation [5]

where \( \phi \) is the ion fluence, \( N_d \) is the number of defects created, and \( \rho \) is the atomic density, meaning the number of atoms per volume unit. DPA values were obtained from 2013 SRIM calculations as discussed later.

1.3.4 – Radiation Damage Models

Radiation damage models offer useful calculations to determine the amount of defects created by the source particle. The simplest model for calculating the number of atomic displacements due to an incident particle is known as the Kinchin-Pease model [40] [5]. In the model, the energy of the knock-on atoms is given as \( (T) \) with the number of atomic displacements represented as \( v(T) \). Its basic assumptions are:

The Kinchin-Pease model derivation ends with the resulting equations,

\[
\begin{align*}
V(T) &= 0 \quad \text{for} \quad T < E_c \\
V(T) &= 1 \quad \text{for} \quad E_d < T < 2.5E_d \\
V(T) &= \frac{T}{2E_d} \quad \text{for} \quad 2.5E_d < T < 2.5E_c \\
V(T) &= \frac{E_c}{2E_d} \quad \text{for} \quad T \geq E_c
\end{align*}
\]

Figure 1.3.6 - Basic assumptions for Kinchin-Pease model [5]
where $E_c$ is cutoff energy. This function is shown in Figure 1.3.7. The Kinchin and Pease model forms a basis for several further refinements, primarily involving calculation of damage energy and a more realistic estimate of the displacement limit.

![Figure 1.3.7](image.png)

Figure 1.3.7 The number of displaced atoms in the cascade as a function of PKA energy according to the model of Kinchin and Pease (Chapter 17) [4]

Modern computer software programs, such as the Stopping Range of Ions in Matter (SRIM) software, use the Norgett-Robinson-Torrens (NRT) modification of the Kinchin-Pease model for defect production. This modification used binary collision computer simulations of ion collisions in solid to demonstrate that about 20% of the sites from where an atom is kicked out are then refilled by another atom. This resulted in a prefactor of 0.8 being introduced to the Kinchin-Pease equation. SRIM software currently remains the most common software for the analysis of ion beam radiation interactions with either monoatomic or multiatomic targets.[41] The SRIM software can quickly output computational data of the interaction between the selected ions and target and generate results on the probable damage cascade, defects produced, and depth of damage.[41], [42] [43]
1.4 Radiation Damage

1.4.1 Fundamentals of Radiation Damage

The characteristics of the damage caused by radiation induced disorder are the focus to test the resistance crystalline materials to become amorphous. To cause a variety of point defects such as vacancies and self-interstitials, atoms must be displaced from their equilibrium locations in the crystal structure by incoming radiation, which is the nature of radiation damage. In addition to neutron irradiation, incoming electrons and ions can also cause this; in research modeling neutron-induced radiation damage, the latter species are frequently utilized. The most important issue requiring more in-depth studies is the need for an understanding of the radiation-induced structural changes at the atomic, microscopic, and macroscopic levels, and the effects of these changes on the release rates of radionuclides during corrosion.

The effect of irradiation on materials is rooted in the initial event in which an energetic projectile strike as discussed previous via PKA. While the event is made up of several steps or processes, the primary result is the displacement of an atom from its lattice site. This section will address primarily crystalline solids in which the atom locations are defined by the crystalline structure. Irradiation displaces an atom from its site, leaving a vacant site behind (a vacancy) and the displaced atom eventually comes to rest in a location that is between lattice sites, becoming an interstitial atom. The vacancy-interstitial pair is central to radiation effects in crystalline solids and is known as a Frenkel pair (FP). The presence of the Frenkel pair and other consequences of irradiation damage determine the physical effects, and with the application of stress, the mechanical effects of irradiation. The radiation damage event, detailed in Ch.2.3 of this report, is concluded when the displaced atom (also known as the primary knock-on atom, PKA) comes to rest in the lattice as an interstitial. Subsequent events are classified as physical effects of irradiation. These effects include such phenomena as swelling, growth, phase change, segregation, which results in disorder of a once ordered material.
1.3.2 Displacement Damage

When hit by high energy ions, ceramic materials undergo displacement damage (DD) through the creation of vacancies, interstitials (Frenkel defects), and dislocation loops.[44] These can result in changes of material properties such as the surface potential, surface conductivity, and mobility [45]. Displacement damage for ceramic materials occurs in functional ceramics due to nuclear collisions.

![Diagram showing primary radiation damage events in material][3]

However, as illustrated in Figure 7 showing the results of molecular dynamics, considerable recovery of displacement damage in ceramics occur due to the mobility of point defects and atoms. Figure 7 further illustrates several primary radiation damage events that occur.

1.3.3 Radiation Damage of Pyrochlore

Radiation creates amorphization, and amorphization creates an ordered to disordered transformation. The two reactions that are required to define this transformation in fluorite are (1) a cation antistite defects must form on the cation sublattice, and (2) anion frenkel defects must be created on the anion sublattice. These defects are the same for fluorite structural derivative oxides exposed to irradiation such as pyrochlore. These reactions are the ordered to disorder (O-D) fluorite defect reaction pair shown in Fig 8. [6]
Cation and anion Frenkel pairs are originally induced by radiation (forward arrows in the reactions above). A Frenkel pair consists of an interstitial and a vacancy (an i–v pair) on either the cation or anion sublattice. Radiation damage evolution is determined by the fate of these i–v pairs. Many annihilate harmlessly, either during the quench of a displacement cascade, or when mobile point defects (usually interstitials) encounter and recombine with their i–v counter parts in the lattice (hence, the reverse arrows in the reactions above). Albeit i–v recombination can be kinetically inhibited and thus some cation and anion Frenkel defects will accumulate in the lattice as radiation damage progresses eventually leading to full amorphous material. [6] This O–D fluorite defect reaction pair is a global descriptor for the nature of O–D transformations across the entire range of oxygen-deficient fluorite structure such as pyrochlore. [6]

In contrast, the pyrochlore structure $A_2B_2O_7$ has remarkable elemental versatility, which makes these materials of considerable interest for the immobilization of actinide-rich nuclear waste and a concept for radiation resistance materials[46]. To resist the cascading defect that radiation induced disorder causes, actinides and lanthanides are incorporated on the A-site and Zr occupying the B-site have been studied extensively. Rare-earth zirconates $A_2Zr_2O_7$ ($A =$ Lanthanide) crystallize in pyrochlore structure as a result.
of their proper radius ratio between $A$-site and Zr-site cations ($1.46 < \frac{r_A}{r_{Zr}} < 1.78$) and have displayed radiation tolerance to some degree.[47], [48] The oxygen vacancy ($V_O$) is the predominant point defect in pyrochlore rare-earth zirconates acting as effective sinks on absorbing or annihilating radiation-induced point defects. and is generally produced during crystal growth[49]

XRD can be used to test the phase loss after irradiation. Techniques such as Grazing Incidence X-ray diffraction (GIXRD) can be used to calculate the depth of the amorphous layer that is caused by such radiation on a crystalline sample. Transmission Electron Microscopy (TEM) can also be used to analyze pyrochlore samples after radiation to see phase stability or amorphization after irritation.

1.3.4 Amorphous Formation

According to basic defect formation models [50], the amorphization takes place, when the number of displaced atoms in unit volume reaches the atomic concentration, meaning all atoms are displaced. During irradiation, simultaneous damage recovery processes mitigate the production of radiation damage, and the rate of damage evolution (e.g., amorphization) will depend on the relative magnitude of these two processes under the irradiation conditions at any given time. For irradiation-induced amorphization, these recovery processes may be associated with point defect migration and annealing in the crystalline state, defect, and ion migration in the amorphization state, or epitaxial recrystallization at the crystalline/amorphous boundaries. Obviously, if the rate of amorphization is less than the rate of the recovery processes, amorphization cannot proceed.

Although the exact nature of the amorphization process is not well defined, amorphization appears to occur by several possible mechanisms (1) in the recoil displacement cascade, (2) from the local accumulation of high defect concentrations due to the overlap of recoil cascade, or (3) by composite or collective phenomena involving more than one process. This radiation-induced amorphization leads to decrease in atomic density and changes in local and long-range structure, which can have a profound effect on the performance and properties of the materials.
CHAPTER 2. EXPERIMENTAL PROCEDURE

2.1 Materials

Materials were chosen in order to best produce single phase titanate pyrochlore and incorporate the lanthanide group as discussed previously in this paper. High purity chemicals were obtained from Alfa Aesar or Sigma-Aldrich (at least 99.9% purity). Pyrochlore was synthesized from powder with equal ratios of 3+ cations on the A site from the lanthanide group. Including Lanthanum, Neodymium, Samarium, Europium, Gadolinium, Dysprosium, Holmium, and Erbium. To keep this ratio equal, with the rutile titanium for the B site, an equation was balanced to calculate weight percent of each starting material to begin synthesis via ball milling. An example of a 5-component titanate pyrochlore calculation to ensure ratios are as precise as the significant figures on our scale.

\[
\begin{align*}
\text{TiO}_2 + \text{Sm}_2\text{O}_3 + \text{Eu}_2\text{O}_3 + \text{Gd}_2\text{O}_3 + \text{Dy}_2\text{O}_3 + \text{Ho}_2\text{O}_3 & \rightarrow (\text{SmEuGdDyHo})_2\text{Ti}_2\text{O}_7 \\
\text{TiO}_2 & \rightarrow 79.9(2) = 159.73 \\
\text{Sm}_2\text{O}_3 & \rightarrow 348.8(1/5) = 69.76 \\
\text{Eu}_2\text{O}_3 & \rightarrow 351.9(1/5) = 70.39 \\
\text{Gd}_2\text{O}_3 & \rightarrow 362.4(1/5) = 72.48 \\
\text{Dy}_2\text{O}_3 & \rightarrow 325.0(1/5) = 74.60 \\
\text{Ho}_2\text{O}_3 & \rightarrow 377.9(1/5) = 75.57 \\
\end{align*}
\]

\[
\text{TiO}_2 \rightarrow 79.9(2) = 159.73 \\
\text{Sm}_2\text{O}_3 \rightarrow 348.8(1/5) = 69.76 \\
\text{Eu}_2\text{O}_3 \rightarrow 351.9(1/5) = 70.39 \\
\text{Gd}_2\text{O}_3 \rightarrow 362.4(1/5) = 72.48 \\
\text{Dy}_2\text{O}_3 \rightarrow 325.0(1/5) = 74.60 \\
\text{Ho}_2\text{O}_3 \rightarrow 377.9(1/5) = 75.57 \\
\]

---

Added masses: 522.53

Equation 2.1.1 – Batch Calculation for Starting Materials
Weight percent was then calculated in correspondence to the total atomic weight of the composition to give a percent of each starting material. Thus, each starting composition is divided by the added masses.

\[
\text{TiO}_2=0.3057 \quad \text{Sm}_2\text{O}_3=0.1335 \quad \text{Eu}_2\text{O}_3=0.1347 \quad \text{Gd}_2\text{O}_3=0.1387 \quad \text{Dy}_2\text{O}_3=0.1428 \quad \text{Ho}_2\text{O}_3=0.1447
\]

The sesquioxide and rutile phase were then massed and recorded giving a 10-gram batch for each composition.

\[
\text{TiO}_2=3.057 \quad \text{Sm}_2\text{O}_3=1.335 \quad \text{Eu}_2\text{O}_3=1.347 \quad \text{Gd}_2\text{O}_3=1.387 \quad \text{Dy}_2\text{O}_3=1.428 \quad \text{Ho}_2\text{O}_3=1.447
\]

A program was written in MATLAB to aid this calculation which can be referenced in the Index.

2.1.1 Traditional Ceramic Processing

The pyrochlore samples were fabricated through traditional ceramic sintering. Prior to starting this process, all powders were dried for two hours in an KSL-1200X-UL Muffle Furnace at 200 °C to remove any existing moisture. Then, the powders were removed from the furnace and massed into the appropriate amounts to achieve a desired composition. The powder mixture is then poured into a zirconia vessel and secured into an 8000D Mixer/Mill® Dual High-Energy Ball Mill. The powder is milled for a total of three hours until there are no chunks present in the powder mixture. At thirty-minute increments, the mill is stopped so that the powders can be scrapped off the sides of the vessel to break down larger chunks. Then, a Carver press is used to pressed approximately 2-3 grams of milled powder into pellets using a lubricated 13mm die. The powder was subjected to 7 tons of force for 3 minutes before the force was slowly released and the pellets were ejected. Pellets were cold pressed using cindol wax as a lubricant. The pellets were then placed into the UL Standard 1200°C Muffle Furnace set at 1000 °C for twelve hours to be calcined. The oven was set at a heating and cooling rate of 10 °C/min.
The calcined pellets then went through the same high energy milling process described above to achieve a powder. The powder was then pressed into 13 mm pellets once more according to the same procedure described above. No binders were used in the pressing process. Once the pellets were pressed, they were placed into an KSL-1700X-A1P Muffle Furnace set at 1600 °C for 72 hours. The oven was set at a heating and cooling rate of 10 °C/min. After the furnace returned to room temperature, the pyrochlore ceramic samples were obtained.
2.1.2 Spark Plasma Sintering

In comparison with regular sintering, we also use Spark Plasma Sintering (SPS) process. The SPS process was carried out using SPS-515S made by Fuji Electronic Industrial Co. SPS is a synthesis and processing technique that makes sintering and sinter-bonding at low temperatures and in short periods possible by discharging between the power particles surface, and/or secondary in gas discharge and Joule heating [51]. Applying continuous ON-OFF DC pulsed high electric current in a low voltage, with sparking case, it effectively performs a high temperature spark plasma generated at an initial stage of energizing momentarily, and an electromagnetic field by DC pulsed current. The method is a solid compressive and a large pulsed electric current energizing sintering technique that has lately drawn considerable attention as one of the newest rapid sintering methods with accurate energy density control.

![Figure 2.1.3. Schematic of SPS setup](image)

Details of SPS process are introduced in Fig. 10. The milled power was put into a graphite mold (Inner diameter is 13mm and height is 20mm.) Before we put the power into the mold, we wrap the inside of the mold with graphite paper to avoid adhesion between sample and graphite wall. And then we put two small graphite punch on the top and bottom of power. To get a higher density, we pressed the two punches using a cutout tool and applied a large force to a graphite sheet. After preparing the powder samples, we put the graphite mold on the chamber and insert the thermocouple to detect the temperature during
process. In this process, we set the heating rate of 100°C/min until 900°C. Pressure of 5MPa is added to the die at 300°C. Because the heating is so fast, to prevent an overshoot of the final 1000°C sintering temp, the heating from 900-1000°C is programmed to be a slower heating rate. The solution can be a 50% slower ramp rate of 50°C/min until the final sintering temperature is achieved. When the sample achieves the desired temperature, the sample is held at the set temperature for 10min. Finally, the pressure is released, and the sample was cools to below 100°C in 20-30 min naturally, in air temperature. The sintered samples were pellets (13 mm in diameter, 1–4 mm in thickness and 2–6 g in weight). In total, the final samples were densified by SPS at 1000 °C for 5 min at a heating rate of 200 °C min\(^{-1}\) under a uniaxial pressure of 5 MPa.

Figure 2.1.4. SPS Temperature for sintering over time
2.2 Characterization

2.2.1 Density

The density of every fabricated sample throughout this project was calculated via the Archimedes’ method using the following equation,

$$\rho = \frac{\rho_w}{1 - \left(\frac{W_w}{W_a}\right)}$$

Equation 2.2.1 – Calculating Density

where $W_a$ is the sample’s weight in air; $W_w$ is the weight submerged in water; and $\rho_w$ is the density of water ($\rho_w = 1.00 \text{ g/cm}^3$). A Denver Instrument laboratory equipped with an Archimedes density set-up was used with deionized water as the fluid. Samples were tested in either duplicate or triplicate and the averages were used to lower the possible amount of experimental error.

2.2.2.1 X-Ray Diffraction

The crystallinity of the pyrochlore compositions was analyzed by using XRD. A Malvern Panalytical “Aeris” XRD was used for this study and scan parameters consisted of measuring from 10°-80°, a step size of 0.02°, and a step time of 0.686 seconds. Measurements were taken on polished, bulk samples to evaluate the crystalline structure occurring near the surface. Observed crystalline were analyzed and matched using a software called “Highscore PLUS.”

2.2.2.2 Grazing Incidence X-Ray Diffraction

For ex-situ irradiated analysis, a Rigaku instrument was used for precision. A small bulk sample was placed on a zero-background plate (ZBP) to reflect X-rays that didn’t hit the substrate to reflect off at a steep enough angle in order to not be absorbed by the receiver to alter the XRD data.
In equation 2.2.2 we calculating absorption is used to show the x-ray penetration depth of XRD patterns via GIXRD. When x-rays encounter any form of matter, they are partly transmitted or partly absorbed.

\[ I_x = I_0 e^{-\frac{\mu}{\rho} \xi} \]

Equation 2.2.2

\( I_0 \) = intensity on incident x-ray beam and \( I_x \) = intensity of transmitted beam after passing through thickness \( \xi \). The linear absorption coefficient \( \mu \) is dependent on the substance considered, its density, and the wavelength of the x-rays. Because \( \mu \) is proportional to density \( \rho \), the quantity \( \frac{\mu}{\rho} \) is a constant of the material and can be consisted of the weighted average of the mass absorption coefficients of materials (eq 2.2.3)

\[ \frac{\mu}{\rho} = w_1 \left( \frac{\mu}{\rho} \right)_1 + w_2 \left( \frac{\mu}{\rho} \right)_2 + \ldots \]

Equation 2.2.3

For grazing-incidence experiments, the depth of X-ray penetration into the sample depends on an incidence angle (\( \alpha \)). The incidence angles used were 0.5°, 0.75°, 1.0°, 1.5°, and 2.0° at a wavelength of 1 A. For calculating the depth of penetration of the beam into the sample, it is necessary to calculate the critical angle (\( \alpha_c \)) for total external reflection to occur. [52]

\[ \alpha \approx (2 \delta)^{1/2} = 1.6 \times 10^{-3} \rho \lambda \]

Equation 2.2.4

\( \rho \) is density in g/cm\(^3\), \( \lambda \) is wavelength in A, and \( \delta(1 - n) \) for refractive index (\( n \)). The penetration depth is then calculated from the final two equations. For incidence angle \( \alpha < \alpha_c \), the penetration depth (\( l \)) is given by:
\[ l = \frac{\lambda}{2\pi(\alpha_c^2 - \alpha^2)^{1/2}} \]

Equation 2.2.5

and for \( \alpha > \alpha_c \), the penetration depth \( (l) \) is given by:

\[ l = \frac{2\alpha}{\mu} \]

Equation 2.2.6

where \( \mu \) is the linear attenuation coefficient. The calculated values of penetration depth \( (l) \) from GIXRD can hopefully reveal a change in the differing depths of amorphous layers in a range of entopic differing pyrochlore. Thus, exposing the radiation stability in entropy stabilized oxide/high entropy oxides (HEO). Based on the above equations, the calculated values of penetration depth \( (L) \) for \( \text{Sm}_2\text{Ti}_2\text{O}_7 \) are shown in Figure 3.2. The results indicate that increasing the grazing incidence beam angle \( \alpha \) from just below \( \alpha_c \) to above \( \alpha_c \) increases the depth from several hundreds of angstroms to few thousand angstroms.

Equation 2.2.7 - GIXRD scattering depth in \( \text{Sm}_2\text{Ti}_2\text{O}_7 \)
2.2.4 Scanning Electron Microscopy & Energy Dispersive X-ray Spectroscopy

Polished surfaces of many samples were examined by using SEM (Hitachi SU5000 VP-SEM) with a backscattered electron (BSE) detector and an Oxford Energy EDS system. The bulk pellets were mounted on a 26 mm sample holder using carbon tape. A thin copper tape was wrapped on one end of the sample and connected to the sample holder to allow a path for the electrons to connect to the ground and prevent charging. SEM Images were produced using 15kV and a pressure of 30 Pa. EDS images were produced using a slightly higher voltage (20kV), to get a larger excitation of x-ray peaks. Point and map identification in pair with chemical mapping data was gathered to fully understand the surface morphology and chemical distribution within the glass.

2.2.5 Transmission Electron Microscopy

High spatial resolution direct investigations of microstructures and damage patterns are made using transmission electron microscopy (TEM). These benefits, along with others, make TEM a potent technique for examining irradiation damage in a materials’ structure. This was done in parallel with In-situ radiation in the IVEM-Tandem Facility at the Argonne National Laboratory for ion implantation experiments.
2.3 Ion Beam Radiation

Ion beam radiation is a tool to investigate radiation damage effects and radiation stability in nuclear waste deposits. Ion beam can simulate alpha decay, being a common radioactive decay process in which an atomic nucleus emits an alpha particle, consisting of two protons and two neutrons. This type of decay is characterized by the emission of high-energy particles, leading to localized radiation damage in the surrounding materials thus ion beam radiation provides an effective means of replicating the radiation damage caused by alpha decay. Energy intensity, ion type, and temperature can all be parameters controlled by experimental environment. Varying radiation doses and energies on different materials, can be paired with TRIM simulation to provide a better understanding of microstructure evolution during characterization via TEM or GIXRD.

2.3.1 Ex-situ radiation

To prepare for Ion beam radiation, samples are polished down to a 1-micron level using diamond lapping paper and diamond suspensions allow for the attainment of a smooth and uniform surface, facilitating accurate and consistent ion beam irradiation. Ex-situ radiation was completed at the University of Texas A&M. Ion accelerating voltage of [Ar] can be varied to allow for damage over a range of depths thus achieving what would be considered bulk damage in a very thin section of the material. [Ar] can also be a penultimate simulant for fission fragment found in nuclear waste forms and nuclear fuel. Radiation damage can be compared to literature through a factor of damage as displacements per atom (dpa). DPA for ion beam tests involves considering the energy, temperature, and ion type which can all be varied during the controlled designed experiment.

\[
DPA = \left( \frac{E}{Ed} \right) * N
\]

Equation 2.3.1 – Displacement per atom
E is the ion energy in joules, Ed is the displacement energy in joules, and N is the atomic density of the material in atoms per cubic meter. temperature adjustment factor (adjusting for temperature) and displacement efficiency factor (adjusting for ion type) is used to modify the DPA value. DPA will be calculated later in the study via TRIM.

Ions penetrate a sample's surface at varying depths allowing for characterization on a bulk pellet to obtain microstructure evolution by studying radiation depth by GIXRD. This approach mimics typical radiation damage caused by alpha particles, which occurs throughout the waste form or fuel rather than solely at the surface. In table 2.3.1, fluence is varied amongst three different samples containing different amounts of lanthanides in the A position.

### 600 KeV [Ar] Irradiations

<table>
<thead>
<tr>
<th>FLUENCE</th>
<th>1 × 10^{14}</th>
<th>5 × 10^{14}</th>
<th>1.5 × 10^{15}</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-1</td>
<td>2-1</td>
<td>3-1</td>
<td></td>
</tr>
<tr>
<td>1-2</td>
<td>2-2</td>
<td>3-2</td>
<td></td>
</tr>
<tr>
<td>1-3</td>
<td>2-3</td>
<td>3-3</td>
<td></td>
</tr>
</tbody>
</table>

1. Sm₂Ti₂O₇
2. (EuGdSm)_₂Ti₂O₇
3. (EuGdSmHoDy)_₂Ti₂O₇

Table 2.3.2: List of samples Ex-Situ Irradiated samples
2.3.2 In-Situ radiation

In-situ Ion irradiation and Transmission Electron Microscopy was performed at the Argonne National Laboratory. The Hitachi 8100 was operated at 300 kV to obtain 1 keV Kr ions for irradiation. Ion irradiations were performed in the IVEM Facility at Argonne National Laboratory in DuPage, Illinois. Sample Preparation requires focused ion beam (FIB) milling. Electron transparent sample thickness is necessary for TEM analysis and to allow electron transmission.

The IVEM Facility offers ion irradiation capabilities, allowing precise control over the energy, fluence, and species of ions used for irradiation. This process induces defects and structural modifications within the crystalline sample simulating radiation damage and TEM allows real-time imaging and analysis of materials under controlled environments and response to specific external inducements. Diffraction analysis using selected-area electron diffraction (SAED) or convergent beam electron diffraction (CBED) techniques provide information about the crystallographic orientation and lattice parameters of the sample. Radiation-induced defects can thus be measured in DPA, given Ion source, time, and temperature to access a specific energy to change phase and lose crystallinity.

Because of the nature of In-Situ TEM sample size, the damaged layer cannot be analyzed in the same practice as GIXRD. The sample thickness of an electron transparent Focused Ion Beam (FIB) sample, discussed later, is around 200 nm. This has to be considered when examining the Displacements per atom and Ion concentration curves after TRIM/SRIM simulation and comparing them the results. Any radiation will pass all the way through the sample.

2.2.3 Radiation Dose Calculation via TRIM

Computational calculations were executed with the 2013 TRIM/SRIM computer code. They were used for characterizing radiation damage due to radiation via dose and penetrations depth. The code performs computational analysis by building models of possible outcomes by substituting a probability distribution
for factors of inherent uncertainty[53]. Then, it calculates a possible outcome multiple times by using a different set of random numbers as input in the probability functions. In the 2013 SRIM code, target layers with specified chemical compositions and densities are customized while controlling the nature of the ion, ion- beam energy, and incident angle. Distinctive values for elemental displacement, lattice, and surface energies can be selected with 2013 SRIM offering default values for each element, if needed. Output text files include information on the ion ranges in the material, backscattered ions,

![Image of 2013 SRIM setup window](image)

Figure 2.2.1: Example of 2013 SRIM setup window for 1000 keV Kr irradiation of

$$(\text{EuGdSmHoDy})_2\text{Ti}_2\text{O}_7$$

transmitted ions, sputtered atoms, and collision details with depth distribution of elemental vacancies created. For the calculations of each material, irradiation damage from a total of 10,000 ions was calculated for each ion. The general 2013 SRIM window for setting the irradiation conditions is illustrated in Figure 9 for the 1000 keV Kr irradiation of $(\text{EuGdSmHoDy})_2\text{Ti}_2\text{O}_7$. 
There are several assumptions contained within the 2013 SRIM code. It assumes the incident ion beam as a flow of individual particles, without considering the dimensions of the ion beam or the spatial distribution of ions in the beam or any type of effects of an earlier ion with the new ion under calculation. Also, it assumes an amorphous structure, thus no crystallographic effects are considered and assumes that ion irradiation occurs at 0 K. In parallel, no thermal effects from the incident beam energy are accounted for, thus there is no diffusion and no self-healing of the structure. Also, 2013 SRIM assumes a constant displacement, lattice, and surface energy value during the process of irradiation. To calculate the effect of ion irradiation on the ceramic pyrochlore, the detailed calculation with full damage cascades option was selected (top right of Fig. 9). The use of the full damage cascade option allows for advanced outputs of irradiation damage including specific vacancy production by target material elements and detailed sputtering calculations. These advanced outputs provide a detailed picture of the calculated irradiation damage. The atomic stoichiometry was calculated to be even for all A components as seen in figure 9.
CHAPTER 3. RESULTS AND DISCUSSION

3.1 Materials and Materials Processing

All the materials were synthesized under conditions listed in the experimental section. Twenty-six samples of twenty-one materials were produced for this study. Green densities obtained by cold-press procedures were typically 70% of theoretical density, and final sintered bulk densities ranged from 70-95% of theoretical density (Table 3.1.1). The different colors of these sintered materials were observed and logged in Table 3.1.1.

Pyrochlore Observation Table

<table>
<thead>
<tr>
<th>1 Component</th>
<th>Density</th>
<th>(% Density)</th>
<th>Single (Pyrochlore) Phase</th>
<th>Observations</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sm$_2$Ti$_2$O$_7$</td>
<td>5.900351526</td>
<td>93.65</td>
<td>Yes</td>
<td>white</td>
</tr>
<tr>
<td>Eu$_2$Ti$_2$O$_7$</td>
<td>5.762874504</td>
<td>90.57</td>
<td>Yes</td>
<td>Yellow tint</td>
</tr>
<tr>
<td>Gd$_2$Ti$_2$O$_7$</td>
<td>6.208298106</td>
<td>94.66</td>
<td>Yes</td>
<td>white</td>
</tr>
<tr>
<td>Nd$_2$Ti$_2$O$_7$</td>
<td>2.897676389</td>
<td>48.09</td>
<td>No</td>
<td>Blue tint</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>2 Component</th>
<th>Density</th>
<th>(% Density)</th>
<th>Single (Pyrochlore) Phase</th>
<th>Observations</th>
</tr>
</thead>
<tbody>
<tr>
<td>(EuGd)$_2$Ti$_2$O$_7$</td>
<td>5.387479391</td>
<td>85.52</td>
<td>Yes</td>
<td>Tan</td>
</tr>
<tr>
<td>(SmGd)$_2$Ti$_2$O$_7$</td>
<td>5.123106266</td>
<td>92.09</td>
<td>Yes</td>
<td>Tan with dark brown spots</td>
</tr>
<tr>
<td>(NdSm)$_2$Ti$_2$O$_7$</td>
<td>5.239680342</td>
<td>84.65</td>
<td>No</td>
<td>Purple tint</td>
</tr>
<tr>
<td>(NdGd)$_2$Ti$_2$O$_7$</td>
<td>5.173084834</td>
<td>82.37</td>
<td>No</td>
<td>Purple tint</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>3 Component</th>
<th>Density</th>
<th>(% Density)</th>
<th>Single (Pyrochlore) Phase</th>
<th>Observations</th>
</tr>
</thead>
<tbody>
<tr>
<td>(EuGdDy)$_2$Ti$_2$O$_7$</td>
<td>4.458389846</td>
<td>69.23</td>
<td>Yes</td>
<td>Tan</td>
</tr>
<tr>
<td>(SmEuGd)$_2$Ti$_2$O$_7$</td>
<td>4.381323081</td>
<td>69.11</td>
<td>Yes</td>
<td>Dark Tan</td>
</tr>
</tbody>
</table>
Table 3.1.1 (above) summarizes the density, pyrochlore phase presence, and visual observations within final ceramic pellets for SPS compositions of interest.

### 3.1.1.1 Fabricated Ceramic Observations - Tradition Ceramic Sintering

Pellets synthesized using Tradition Ceramic Processing (TCP) were sintering in alumina $\text{Al}_2\text{O}_3$ crucibles and appeared to be exceptionally consistent structurally between varying lanthanides used as the $3^+$ cations in the A site of pyrochlore.

<table>
<thead>
<tr>
<th>4 Component</th>
<th>Density</th>
<th>(%) Density</th>
<th>Single (Pyrochlore) Phase</th>
<th>Observations</th>
</tr>
</thead>
<tbody>
<tr>
<td>(SmEuGdDy)$_2$Ti$_2$O$_7$</td>
<td>4.404871331</td>
<td>68.83</td>
<td>Yes</td>
<td>Tan</td>
</tr>
<tr>
<td>(SmEuGdHo)$_2$Ti$_2$O$_7$</td>
<td>4.476422821</td>
<td>69.83</td>
<td>Yes</td>
<td>Tan</td>
</tr>
<tr>
<td>(NdSmEuGd)$_2$Ti$_2$O$_7$</td>
<td>3.105575451</td>
<td>49.37</td>
<td>No</td>
<td>Purple</td>
</tr>
<tr>
<td>(LaSmEuGd)$_2$Ti$_2$O$_7$</td>
<td>3.619735474</td>
<td>57.92</td>
<td>No</td>
<td>Tan with dark brown spots</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>5 Component</th>
<th>Density</th>
<th>(%) Density</th>
<th>Single (Pyrochlore) Phase</th>
<th>Observations</th>
</tr>
</thead>
<tbody>
<tr>
<td>(SmEuGdDyEr)$_2$Ti$_2$O$_7$</td>
<td>4.99200771</td>
<td>77.28</td>
<td>Yes</td>
<td>Pink</td>
</tr>
<tr>
<td>(SmEuGdDyHo)$_2$Ti$_2$O$_7$</td>
<td>4.5055102</td>
<td>70.30</td>
<td>Yes</td>
<td>Tan</td>
</tr>
</tbody>
</table>

Table 3.1.1 – Pyrochlore Observations (More data continued in Index)
Figure 3.1.1 and figure 3.1.2, (Sm)\textsubscript{2}Ti\textsubscript{2}O\textsubscript{7} and (NdGd)\textsubscript{2}Ti\textsubscript{2}O\textsubscript{7} respectively are images after calcination. The pellets appear smooth and will leave a powdery residue if touched. The final sintered density decreases...
with addition of cations to the A-position and is discussed in detail later. The pellets were polished from high grit sandpaper to 0.3-micron diamond lapping paper to produce a smooth surface as seen in figure 3.1.5 and figure 3.1.6.

3.1.1.2 Fabricated Ceramic Observations – Spark Plasma Sintering

Similar to TCP the color is dependent on the variety of lanthanides that were used that displayed which were diverse in color. Fig. 3.1.8 and Fig. 3.1.9 show polished pellets that can be seen to vary in color due to the presence of a different series of lanthanides. There does appear to be to 1 mm size dots of discoloration. As seen there is a consistent color gradient that gets darker towards the edges of the pellet.

Fig. 3.1.7 optical Microscope image of a polished (SmEuGdDyHo)\(_2\)Ti\(_2\)O\(_7\) surface prepared by SPS

Fig. 3.1.8 (SmEuGd)\(_2\)Ti\(_2\)O\(_7\)  
Fig. 3.1.9 (SmEuGdDyHo)\(_2\)Ti\(_2\)O\(_7\)
3.1.2 Density

Density was collected via Archimedes method and can be analyzed in table 3.1 and in supplementary information. The trend with the addition of cations to the A-position of pyrochlore is a decrease in density.

Atomic size and packing of the added cations ranging from 2.57 angstroms (Ti) to 2.80 angstroms (Sm) may lead to alterations in the atomic arrangement. Also, localized areas of porosity or voids can form, contributing to a decrease in density which can later be seen through Scanning Electron Microscopy. Clashing lattice systems due to slight variance in sintering temperatures or cooling times per cation response to forming pyrochlore with Titanium can further disrupts atomic arrangement contributing to a reduction in ceramic density.

![Pyrochlore density by with varying A- Component](image)

**Figure 3.1.1 - Pyrochlore density by with varying A- Component**

Furthermore, Spark Plasma Sintering can decrease in sintering times and temperatures observed to further enhance the density among solid solution ceramics (Figure 3.1.1). SPS employs the simultaneous
application of high pressure and pulsed direct current (DC) or radio frequency (RF) heating, which allows for rapid and efficient densification of materials. The combination of pressure and high heating rates enables enhanced mass transport, reducing diffusion distances and promoting densification.\[54\]

SPS typically operates at lower temperatures compared to conventional ceramic processing methods such as hot pressing or sintering. The lower temperatures help to mitigate grain growth and reduce the risk of phase transformations or chemical reactions that can occur at higher temperatures, leading to better retention of the desired microstructure and properties. Because of the slight differences in cations consuming the A- position, 3 and 5 component SPS prepared pyrochlore displayed an average of 14% higher density when compared to pyrochlore prepared by Tradition ceramic processing. This can be attributed to the combination of rapid heating, efficient densification, lower sintering temperatures, uniform pressure application, and precise control over sintering parameters makes.
3.1.3 X-Ray Diffraction

Ceramic pellets were analyzed via XRD after sintering. XRD patterns either confirm single pyrochlore phase within a composition or provide data to extrapolate multiple phases after the final sinter. Although final sintering temperature was altered between 1450°C - 1650°C for some samples, all samples were calcined at 1000 degrees C° for 12 hours first and the synthesized by the same method before the final sinter. Pyrochlore could be indexed with powder diffraction data (ICSD# 413013) and High-Score data software. All data shown in table 3.1.1 is collected via bulk samples. Single phase pyrochlore was achieved with 1,2,3,4 and 5 cations in the A position at varying temperatures (Table 3.1.1).

![Eu2_Ti2_O7 XRD](image)

Eu2Ti2O7 shown in figure 3.1.7 was sintered at 1600 C° for 72 hours and displays singles phase pyrochlore with discernible peaks; evident peaks include the highest intensity at 30 degrees (222) and at 15 degrees (111). Four different cations were used for Single component synthesis with final sintering temperatures ranging from 1450C°-1650C° (Table 3.1.1) all with discernable pyrochlore peaks except for Nd2Ti2O7. It is observed that pellets containing Neodymium in the A position, with or without other cations present, always resulted in initial mixing phases also being present in the end product. For instance, in
(NdSm)$_2$Ti$_2$O$_7$, the diffraction patterns of the sesquioxide phase, Nd$_2$O$_3$ (cubic) and the rutile phase, TiO$_2$ (monoclinic) are both present along with the pyrochlore diffraction pattern (Fig 3.1.8). The presence of these original phases gives rise to the understanding that the Sm$_2$O$_3$ sesquioxide phase is also present. There is another subphase present, Nd$_2$TiO$_5$, showing that neodymium is resistance the pyrochlore phase.

![Nd_Sm_Ti2_O7](image)

*Fig. 3.1.8 – X-Ray Diffraction Pattern of (NdSm)$_2$Ti$_2$O$_7*

(NdSm)$_2$Ti$_2$O$_7$ was synthesized with a final sintering temperature of 1600°C for 72 Hours. This was confirmed in literature [16] [55] [56] and the use of Neodymium or Lanthanum produces mixed final phases, differing than other lanthanides tested in this study to fabricate pyrochlore phase with the same sesquioxide and rutile starting materials. All other two A-component pyrochlore portrayed a pyrochlore diffraction pattern as (SmGd)$_2$Ti$_2$O$_7$ shown in figure 3.1.9.
As more components were added to the A position, most compositions were held at 1600°C for 72 hours for the final sinter. (SmEuGd)\textsubscript{2}Ti\textsubscript{2}O\textsubscript{7} was synthesized at 1500°C and 1600°C to show that grains were still able to grow with varying final sintering temperature (Figure 3.1.10)

Figure 3.1.10 – (SmEuGd)\textsubscript{2}Ti\textsubscript{2}O\textsubscript{7} final sintering temperature 1500°C and 1600°C respectively
With four components in the A position, varying sized cations made it more challenging to synthesis in a single phase. Moreover, (HoEuGdSm)\textsubscript{2}Ti\textsubscript{2}O\textsubscript{7} displays a single phase with a final sintering temperature of 1600 C° for 72 hours. (Fig 3.1.11)

![Graph](image1)

Fig 3.1.11 - (HoEuGdSm)\textsubscript{2}Ti\textsubscript{2}O\textsubscript{7}

The five-component titanate, (LaNdSmEuGd)\textsubscript{2}Ti\textsubscript{2}O\textsubscript{7}, resembled similar behavior to (NdSm)\textsubscript{2}Ti\textsubscript{2}O\textsubscript{7} with a multiphase system after the final sinter of 1600 C° for 72 hours (Fig. 12).

![Graph](image2)

Fig 3.1.12 - (LaNdSmEuGd)\textsubscript{2}Ti\textsubscript{2}O\textsubscript{7} phases present
Furthermore, two other compositions of five component pyrochlore were synthesized at a final sinter of 1600°C for 72 hours in single phase being (EuGdErDySm)$_2$Ti$_2$O$_7$ and (SmDyHoEuGd)$_2$Ti$_2$O$_7$. A second attempt to process these 5-component single phase pyrochlore with a shorter final sintering time (48 hours instead of 72 hours) was successful, while narrower peaks inform grain size is sacrificed with decrease crystallite size (Figure 3.1.13).

![Graph](image_url)

Fig 3.1.13-(SmEuGdDyHo)$_2$Ti$_2$O$_7$ (above) & Fig 3.14 (SmEuGdDyEr)$_2$Ti$_2$O$_7$ (below) different times

![Graph](image_url)

Figure 3.1.14 – SPS (SmGdEuDyHo)$_2$Ti$_2$O$_7$ XRD

Two five component samples were synthesized by SPS which also displayed defined Pyrochlore peaks.
3.1.4 Scanning Electron Microscopy and Energy Dispersive X-ray Spectroscopy

Pyrochlore samples tended to display a homogenous chemical distribution, while crystalline samples present a homogenous distribution of the five cations as synthesized via traditional ceramic processing, with a low contrast on the BSE image and a uniform distribution on the elemental mapping, as shown in figure 3.1.1. The elemental mapping for cations shows a homogeneous distribution of Ti, whereas in figure 3.1.3 and 3.1.4 segregation occurs between the cations on the B-site. This can be classified as sluggish diffusion [57], a phase transformation that depend on atomic diffusion require the cooperative diffusion of elements in order to attain the equilibrium partitioning among the phases. This can also be described as the cocktail effect as a result of having multi-principal-element mixtures are found to be the core factors influencing the microstructure and properties of high-entropy alloys. The Gd rich phase is not seen in the XRD pattern, which can be explained by an insufficient quantity to be detected and/or a poor crystallization.

The introduction of Gd on the B-site of the pyrochlore structure may lead to an increase in enthalpic energy whereas a result during the decomposition process, some lanthanide cations separate from the other cations. It is possible that the lack of consistent separation or segregation observed among Sm, Eu, Dy and Ho suggests that pyrochlores with high entropy, containing only these four cations on the B-site, are likely not stabilized by entropy but instead form a solid solution. [58]
Figure 3.1.1 - SEM/EDS observations of TCP $\text{Sm}_2\text{Ti}_2\text{O}_7$

Figure 3.1.2 - SEM/EDS observations of TCP $(\text{SmGdEuDyHo})_2\text{Ti}_2\text{O}_7$
Figure 3.1.3 - SEM/EDS observations of SPS $\text{Sm}_2\text{Ti}_2\text{O}_7$

Figure 3.1.4 - SEM/EDS observations of SPS $\text{(SmGdEuDyHo)}_2\text{Ti}_2\text{O}_7$
3.2 Ion Irradiation and Radiation Stability Characterization

3.2.1 Grazing Incident Angle X-Ray Diffraction (X-ray penetration) Analysis

Grazing Incident X-ray diffraction (GIXRD) is an advanced technique used to study the structural properties of materials, particularly those subjected to ion irradiation damage [59]. Traditional X-ray diffraction (XRD) methods are limited in their ability to probe the surface layer of materials and provide structural information only from a few micrometers beneath the surface. However, GIXRD overcomes this limitation by employing an oblique angle of incidence of X-rays onto the sample, allowing for the analysis of the surface layer and its changes before and after ion irradiation.

TRIM simulation indicates that rare-earth titinate pyrochlore, when subjected to 600 keV heavy ion irradiation, develops an irradiation damage layer with a peak below 100 nm. By analyzing the diffraction patterns produced by the X-rays grazing the surface of the material, insights into the damaged structure of the material before and after ion irradiation was gained, providing a deeper understanding of the effects of irradiation on the material's properties.

GIXRD is used to obtain surface structural information in a bulk or thin film materials by controlling X-ray incidence angle (in other words, X-ray penetration depth)

3.2.2 Grazing Incident Angle X-Ray Diffraction (X-ray penetration) Technique

The linear absorption coefficient $\mu$ is dependent on the substance considered, its density, and the wavelength of the x-rays.

$$\frac{\mu}{\rho} = w_1 \left( \frac{\mu}{\rho} \right)_1 + w_2 \left( \frac{\mu}{\rho} \right)_2 + \cdots \quad \text{(Equation 3.2.1)}$$

For calculating the depth of penetration of the beam into the sample, it is necessary to calculate the critical angle ($\alpha_c$) for total external refraction to occur.
\[ \alpha \approx (2\delta)^{1/2} = 1.6 \times 10^{-3}\rho^{1/2}\lambda \]  
(Equation 3.2.2)

where \( \rho \) is the density of materials in g cm\(^{-3} \), \( \lambda \) is the wavelength of X-ray in Å, and \( \delta = (1-\eta) \) for refractive index (\( \eta \)). The penetration depth is then calculated by the following equations:

\[ L = \frac{\lambda}{2\pi(\alpha_c^2 - \alpha^2)^{1/2}} \quad (\text{for } \alpha < \alpha_c) \]  
(Equation 3.2.3)

\[ L = \frac{2\alpha}{\mu} \quad (\text{for } \alpha > \alpha_c) \]  
(Equation 3.2.4)

Using \( \text{Sm}_2\text{Ti}_2\text{O}_7 \) for an example, we want to calculate the critical angle using equation 3.2.

\[ 1.6 \times 10^{-3} \times 5.900 \left( \frac{g}{\text{cm}^3} \right)^{1/2} \times 1.54 \]  
(Equation 3.2.5)

\[ .005985 \text{ rad} \times \left( \frac{180^\circ}{\pi} \right) \]  
(Equation 3.2.6)

\[ \text{Critical angle} \rightarrow 0.345^\circ \]

Penetration depth is then calculated with one of the following equations. If \( \alpha > \alpha_c \), the penetration depth \( (l) \) is given by equation 3.7 and for incidence angle \( \alpha < \alpha_c \), the penetration depth \( (l) \) is given by equation 3.8.

\[ l = \frac{2\alpha}{\mu} \]  
(Equation 3.2.7)

\[ l = \frac{\lambda}{2\pi(\alpha_c^2 - \alpha^2)^{1/2}} \]  
(Equation 3.2.8)

Continuing with \( \text{Sm}_2\text{Ti}_2\text{O}_7 \) as an example, calculating penetration depth incident angle of 0.5\(^\circ \). Because this angle (0.5\(^\circ \)) is larger than the critical angle that we calculated being 0.343\(^\circ \) thus we use equation 3.

\[ \frac{2 \times 0.0087412 \text{ rad}}{\left( 184.163 \frac{\mu}{\rho} \times 5.90\rho \right)} \]  
(Equation 3.2.9)
161 nm is the final penetration depth with a 0.5° Incident angle. Notice all angles are converted from degrees to radians before final penetration depth is calculated. Depths for single component pyrochlore and 5 component pyrochlore are shown below in figures in 3.14 and 3.15.

3.2.3 Grazing Incident Angle X-Ray Diffraction (X-ray penetration) Experiment to characterize damaged layer.

In figure 3.2.1 the grazing incident angles can be observed at gamma = .25, .5, .75, 1.0, 1.5, 1.75, and 2 degrees. In table 3.2.1 and 3.2.2, the observed angles can be translated to x-ray penetration depth. Other examined values can help interpret the evolution on the decrease in structure, as the x-rays penetrate a shallower area of the amorphous substrate on top of the crystalline surface. As previously discussed in section 2.2.2.2, X-ray penetration depth can be explained via the Linear absorption coefficient and sample density. These equations along with the density of single A – component pyrochlore (Sm$_2$Ti$_2$O$_7$) and 5 A -component pyrochlore (SmEuGdDyHo)$_2$Ti$_2$O$_7$ and literature values for linear attenuation coefficient portray a damage analysis after ex-situ radiation.

In figures 3.2.1 and 3.2.2, and table 3.2.1 x-rays penetrated Sm$_2$Ti$_2$O$_7$ at a depth of 383 nm after 1.5E15 radiation while displaying full crystallinity loss at 0.25 Grazing Incidence and peak broadening in all grazing incident angles due to the displacement cascade during radiation. Calculation of penetration depth can be seen in an example calculated below and was repeated for all incident angles.

\[
1.6 \times 10^{-3} \times 5.900 \left(\frac{g}{cm^3}\right)^{\frac{1}{2}} \times 1.54
\]

\[
\frac{2 \times 0.0087412 \text{ rad}}{\left(\frac{308.737 \mu}{\rho \times 5.90\rho}\right)} = 95 \text{ nm}
\]

Equation 3.2.10 – Sm$_2$Ti$_2$O$_7$ Penetration depth at 0.5 degree incidence angle (example)
Figure 3.2.1 – Sm$_2$Ti$_2$O$_7$ 1.5E15 Grazing X-ray Diffraction Peaks

Figure 3.2.2 – Sm$_2$Ti$_2$O$_7$ 1.5E15 TRIM simulation with X-Ray Penetration Depth Reference
Figure 3.2.2 – (SmEuGdDyHo)\textsubscript{2}Ti\textsubscript{2}O\textsubscript{7} 1.5E15 TRIM simulation with X-Ray Penetration Depth Reference

Figure 3.2.3 – (SmEuGdDyHo)\textsubscript{2}Ti\textsubscript{2}O\textsubscript{7} 1.5E15 Grazing X-ray Diffraction Peaks
Grazing Incident angle (degrees) to penetration depth (nm)

<table>
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<tr>
<th>angle (degrees)</th>
<th>angle (radians)</th>
<th>penetration depth (nm)</th>
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<tr>
<td>0.25</td>
<td>0.004363323</td>
<td>59</td>
</tr>
<tr>
<td>0.5</td>
<td>0.008726646</td>
<td>95</td>
</tr>
<tr>
<td>0.75</td>
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</tr>
<tr>
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<td>192</td>
</tr>
<tr>
<td>1.5</td>
<td>0.026179939</td>
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</tr>
<tr>
<td>2</td>
<td>0.034906585</td>
<td>383</td>
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</table>

Table 3.2.1 - Sm$_2$Ti$_2$O$_7$

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<tr>
<th>angle (degrees)</th>
<th>angle (radians)</th>
<th>penetration depth (nm)</th>
</tr>
</thead>
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<tr>
<td>0.25</td>
<td>0.004363</td>
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</tr>
<tr>
<td>0.5</td>
<td>0.008727</td>
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<tr>
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</tr>
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<td>1.5</td>
<td>0.02618</td>
<td>466</td>
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<tr>
<td>2</td>
<td>0.034907</td>
<td>622</td>
</tr>
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</table>

Table 3.2.2 - (EuGdSmHoDy)$_2$Ti$_2$O$_7$

In figures 3.2.3 and 3.2.4, and table 3.2.2 x-rays penetrated (SmEuGdDyHo)$_2$Ti$_2$O$_7$ in a depth of 622 nm with much sharper peaks at 15 and 30 when compared to Sm$_2$Ti$_2$O$_7$ at low Incident angles.

The broadening of peaks occurs due to two main factors: first, the loss of long-range order in the amorphous material leads to a distribution of interatomic distances, resulting in a broadening of the
diffraction peaks. Second, the local structural variations, such as bond length fluctuations and coordination number changes, also contribute to peak broadening.

The full width half maximum (FWHM) is a parameter used to characterize the broadening of X-ray diffraction peaks. It represents the width of the peak at half of its maximum intensity. By measuring the FWHM of the diffraction peaks in an amorphous material, one can quantitatively assess the degree of disorder or crystalline order present. Generally, a larger FWHM indicates a greater amount of disorder and a broader distribution of interatomic distances within the material.

In $\text{Sm}_2\text{Ti}_2\text{O}_7$, $\gamma = 2.0$ (Incident angle) corresponds to a penetration depth of 383 nm and $\gamma = 0.5$ corresponds to a penetration depth of 95 nm. The FWHM values at the 222 peaks are 0.3576 and 4.5617 respectively. The broadening of the peaks due to loss in crystallinity may have lead ICCD XRD analysis to merge the peaks FWHM calculation with the adjacent 311 peak enhancing the difference in the comparison of width. In contrast to the difference of 4.2041, in $(\text{EuGdSmHoDy})_2\text{Ti}_2\text{O}_7$, $\gamma = 2.0$ corresponds to a penetration depth of 622 nm and $\gamma = 0.5$ corresponds to a penetration depth of 155 nm. The FWHM values at the 222 peaks are 0.2775 and 0.3120 respectively resulting in a difference of 0.0345.

By comparing the FWHM values of diffraction peaks in the amorphous state with those in the corresponding crystalline state or a reference material, one can further evaluate the extent of structural changes induced by irradiation and assess the amorphization process. The FWHM analysis provides valuable insights into the dis-ordering mechanisms and the structural transformations occurring in materials under irradiation or other forms of structural modification.

GIXRD can be limited in terms of accuracy due to the presence of uncontrolled variables. One of the main challenges is the difficulty in precisely controlling the grazing angle of incidence, which affects the penetration depth of the X-rays into the sample. Variations in the grazing angle can lead to inconsistent
depth profiling and introduce uncertainties in the obtained diffraction patterns. Additionally, surface roughness and sample morphology can significantly influence the diffraction signals. Small inconsistencies in sample orientation can cause misalignment or non-uniformity which introduces distortions in the diffraction data. These uncontrolled variables pose limitations on the accuracy and reliability of GIXRD results, leading to further damage analysis through more refined techniques.

3.2.3.1 Lattice Parameter

The lattice parameter refers to the distance between adjacent lattice points in a crystal lattice structure. It is a fundamental characteristic of crystalline materials and plays a crucial role in determining their physical properties. X-ray diffraction is a widely used technique to measure the lattice parameter accurately. In Bragg's law, the incident X-rays are diffracted by the crystal lattice planes at specific angles, resulting in constructive interference. By measuring the angles and intensities of the diffracted X-rays, a diffraction pattern is obtained. The lattice parameter can be determined by analyzing the positions and intensities of the diffraction peaks in the pattern, using mathematical equations derived from the Bragg's law. The lattice parameter calculated from X-ray diffraction provides valuable information about the crystal structure, symmetry, and composition of materials.

Lattice parameter did not show any significant variance between samples with varying X-ray penetration depths, revealing no peak shift with radiation dose. For reference, the lattice parameter in single component, Sm$_2$Ti$_2$O$_7$ pyrochlore was 10.2187, 10.264, and 10.2335 angstroms at 0.25, 0.5, and 2.0 degrees respectively. (SmEuGdDyHo)$_2$Ti$_2$O$_7$ was 10.1730, 10.1733, 10.1736 angstroms at 0.25, 0.5, and 2.0 degrees respectively.
3.2.3 In-Situ Transmission Electron Microscopy Observation

A FIB (Focused Ion beam) sample was produced for electron-transparency using a SPS prepared \((\text{SmEuGdDyHo})_2\text{Ti}_2\text{O}_7\) pyrochlore sample with help of Saraf Laxmikant at the EML Clemson University (Figure 3.2.1). This sample was sent to IVEM-Tandem Facility at the Argonne National Laboratory for In-Situ TEM characterization.

![Image](image.jpg)

Figure 3.2.1 - \((\text{SmEuGdDyHo})_2\text{Ti}_2\text{O}_7\) FIB sample

A 1.0 MeV Kr+ ion implantation in bulk \((\text{SmEuGdDyHo})_2\text{Ti}_2\text{O}_7\) pyrochlore was performed at room temperature using the tandem ion accelerator at Argonne National Laboratory at a fluence of \(5\times10^{14}\) ions/cm\(^2\). The radiation damage and implanted microstructures were examined using cross sectional and high-resolution TEM techniques with a JEOL JEM 2010F microscope operating at 200 keV. The damage profiles observed by In-Situ TEM were compared with that simulated by SRIM. The critical amorphization dose in the unit of displacements per atom (DPA) was determined as the dose at the front of the amorphous layer created by ion beam damage.
Figure 3.2.2 - SAED patterns of (SmEuGdDyHo)$_2$Ti$_2$O$_7$

It is known that 100,000 counts of 1 MeV Kr correspond to a fluence of 6.3E14 ions/cm$^2$ which is the energy of the particles and the relationship between dose and fluence for that particular radiation type. By 1 MeV Kr radiation, the fluence was calculated by the following equation for 16000 counts.

Figure 3.2.3 TRIM calculation of [Kr] implantation of (SmEuGdDyHo)$_2$Ti$_2$O$_7$
Fluence = 6.3E9 ions/cm² per count * 16,000 counts

\[
Fluence = \frac{6.3 \times 10^9 \text{ions}}{\text{cm}^2} \times 32,000 \text{ counts}
\]

Equation 3.2.1 - Fluence calculation in counts

\[
Fluence = 2.016 \times 10^{14} \text{ ions/cm}^2
\]

Equation 3.2.2 – Fluence calculation in Ions

Therefore, 32,000 counts correspond to a fluence of approximately 2.016E14 ions/cm². Fluence refers to the number of particles passing through a unit area, while dose represents the amount of the energy deposited by these particles in the material. This data shows that there is no radiation stability achieved from pyrochlore material with five A-position cations. This is consistent with the radiation damage study of pyrochlore by Jie Lian on beam implantation and cross-sectional TEM studies of lanthanide titanate pyrochlore. [7]

Jie Lian’s study (figure 3.2.6) shows a trend in observed critical amorphization doses for different titanate pyrochlores at room temperature. The scatter in the baseline critical amorphization dose may result from the experimental uncertainty in determining the critical amorphization fluences during in-situ TEM observation. Titanate pyrochlores are generally sensitive to ion beam damage, and relatively low ion fluences were required to fully amorphize these materials. Cross-sectional TEM analysis was able to display a consistent trend as a function of ionic radius of the A-site cation for this study. This research given a reference for the amorphization dose for ordered pyrochlore to be within .11 - .229 DPA in pyrochlore with cations in the A-position with decreasing Ionic radius (Sm 1.78 – to Er 1.66).
The critical amorphization doses (open circles) for 1 MeV Kr+ implantation at room temperature as a function of cation ionic radius ratio, rA/rB, of the titanate pyrochlore A2Ti2O7 single crystals (A = Sm, Eu, Gd, Dy and Er). Data (open squares) obtained by in situ TEM studies [18] are included for comparison.[7]

With consistent parameters and similar radiation doses, there is proof that the radiation damage resistance does not improve with the addition of multiple cations to the A- position of a pyrochlore ceramic with equiatomic proportions. This also gives evidence to the structure study conducted via GIXRD earlier in this research does yield inconclusive results.
CHAPTER 4. CONCLUSIONS AND FUTURE WORK

4.1 Conclusions

Lanthanide titanate pyrochlore $A_2\text{Ti}_2\text{O}_7$ (A-Lanthanide) was successfully produced by TCP and SPS. Radiation damage studies have proved that with increasing cations to increase entropy of a system, there is no improved resistant to damage induced by radiation. Microstructural evolution due to ion beam damage was examined by in-situ TEM and compared to accredited studies in literature. The critical amorphization doses at room temperature are derived by comparing the experimental damage profiles with those simulated by SRIM.

GIXRD studies where inaccurate and produced faulty results due to possible inaccuracies in angle control of the incident X-ray beam leading to a steeper penetration depth than assumed. This displayed higher crystallinity than originally presumed for a radiation stability test.

4.2 Future work

4.2.1 Synthesis

Various fabrication techniques have been optimized for the fabrication of HEO pyrochlores. These techniques include Spark Plasma Sintering and Hot pressing “Veerle Keppens et al.”. Furthermore, techniques such as single crystal growth and sol-gel methods can be explored to optimize the synthesis process and achieve desirable properties including a high density and single phase. Likewise, single crystal five-component pyrochlore was successfully grown using the floating-zone growth technique and a two-mirror optical floating-zone furnace (Canon Machinery model SC1-MDH) with 1500-W halogen lamps. “Veerle Keppens et al.” [60] Some of these experiments have yielded high density albeit further experimentations can enhance all processes leading to single phase fabrication of muti-component systems.
Because fabrication multicomponent pyrochlore lattice is has considerable room for improvement, if done systematically, adjustments in ratios and types of cations in the pyrochlore structure can support an understand of how the composition affects the material's radiation tolerance. Because multicomponent materials typically possess heavily distorted lattices and improved chemical durability, these materials can be highly attractive for radiation applications [61] and should continue to be investigated for radiation damage studies even if increasing entropy is not a defining factor of increasing stability of multi-component pyrochlore.

4.2.2. Characterization of Radiation Damage

With more time it would be important to implement more characterization techniques on irradiated samples. In-situ TEM is an important technique but cross-sectional TEM in ex-situ radiated samples “Jie Lian, Rod Ewing et al.” could improve the study the radiation damage effects on HEO pyrochlores. Investigate the radiation response of HEO pyrochlores under different irradiation conditions, including varying ion energies, fluences, and irradiation temperatures can help bring significance to structural changes and material degradation mechanisms.

Property-performance correlations can establish correlations between the microstructure, composition, and radiation resistance of HEO pyrochlores. Defect concentration, crystallographic structure, and phase stability can be further investigated in parallel withstand radiation-induced damage [62]. This will aid in designing HEO pyrochlores with tailored properties for specific applications in radiation environments.

Modeling and Simulation would need continue to be used to clarify defect formation energies, defect diffusion, and defect clustering, providing a deeper understanding of the radiation response of these materials for the future application potential of waste formations for radioactive waste immobilization.
4.2.3. Thermal dynamic studies

Mechanical and thermal properties of HEO pyrochlores could permit more insight on the enthalpy of formation and thus the Entropy of the system to see if the addition of cations to the A-site of pyrochlore or other theoretical entropic enhancement is truly being achieved during the fabrication process of crystalline materials (in this case being pyrochlore specifically). Investigation of changes in mechanical strength, hardness, thermal conductivity, and thermal stability before and after radiation exposure would possibly assess the impact of radiation damage on these properties.
References


U. Diebold, “The surface science of titanium dioxide.”


[58] F. Vayer, C. Decorse, D. Béardan, and N. Dragoe, “New entropy-stabilized oxide with pyrochlore structure: Dy2(Ti0.2Zr0.2Hf0.2Ge0.2Sn0.2)2O7,” *J Alloys Compd*, vol. 883, Nov. 2021, doi: 10.1016/j.jallcom.2021.160773.


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<th>Single Pyrochlore Phase</th>
<th>Sintering Method</th>
<th>Density Range</th>
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<th>Theoretical Density</th>
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<tr>
<td>(LaNdSmEuGd)2Zr2O7</td>
<td>5.97029787</td>
<td>1000</td>
<td>0.1</td>
<td>Yes</td>
<td>SPS</td>
<td>5.80-6.14</td>
<td>5.97</td>
<td>7.3</td>
<td>81.78% light purple with white splotches</td>
<td></td>
</tr>
</tbody>
</table>
Equations

\[ S_{\text{Config}} = -R \left[ x \left( \sum_{a=1}^{M} x_a \ln (x_a) \right)_{\text{cation site}} \right] \]

Equation 1.2.1. Configurational entropy \((S_{\text{Config}})\) of single cation sub-lattice (fluorite) 18

\[ S_{\text{Config}} = -R \left[ x \left( \sum_{a=1}^{M} x_a \ln (x_a) \right)_{A-\text{site}} + y \left( \sum_{b=1}^{N} y_b \ln (y_b) \right)_{B-\text{site}} + z \left( \sum_{o=1}^{P} z_o \ln (z_o) \right)_{C-\text{site}} \right] \]

Equation 1.2.2. \(x_a, y_b\) and \(z_o\) being the mole fractions of the elements present in the A-site, B-site and \(O^2-\)site (or anion site), respectively. While \(M, N\) and \(P\) are the number of cations present on A-sites, B-sites and anions on \(O^2-\)sites, respectively. 19

\[ R = \int_{0}^{E_0} S^{-1} dE \]

Equation 1.2.3 - The general expression for the range of ions in solids. [33] 22

\[ S = S_n + S_e \]

Equation 1.2.4 – Total electron stopping power [33] 22

Equation 2.1.1 – Batch Calculation for Starting Materials 33

Equation 2.2.1 – Calculating Density 39

Equation 2.2.2 – 6 41
\[ DPA = \left( \frac{E}{Ed} \right) * N \]

Equation 2.3.1 – Displacement per atom

Equation 3.2.1 – 9 Calculating Penetration depth for GIXRD

Equation 3.2.10 – Sm2Ti2O7 Penetration depth at .5 degree incidence angle (example)

\[ Fluence = \frac{6.3 \times 10^9}{cm^2} * 32,000 \text{ counts} \]

Equation 3.2.1 - Fluence calculation in counts

\[ Fluence = 2.016 *14 \text{ ions/cm}^2 \]

Equation 3.2.2 – Fluence calculation in Ions