

Thermophysical Properties and Radiation Damage of NdCrO₃ and NdAlO₃

Author:

Guo, Rui

Publication Date:

2016

DOI:

<https://doi.org/10.26190/unsworks/18981>

License:

<https://creativecommons.org/licenses/by-nc-nd/3.0/au/>

Link to license to see what you are allowed to do with this resource.

Downloaded from <http://hdl.handle.net/1959.4/56120> in <https://unsworks.unsw.edu.au> on 2024-05-01

Thermophysical Properties and Radiation Damage of NdCrO_3 and NdAlO_3

Rui Guo

A thesis in fulfilment of the requirements for the degree of

Master of Engineering



School of Materials Science and Engineering

Faculty of Science

University of New South Wales

February 2016

ORIGINALITY STATEMENT

'I hereby declare that this submission is my own work and to the best of my knowledge it contains no materials previously published or written by another person, or substantial proportions of material which have been accepted for the award of any other degree or diploma at UNSW or any other educational institution, except where due acknowledgement is made in the thesis. Any contribution made to the research by others, with whom I have worked at UNSW or elsewhere, is explicitly acknowledged in the thesis. I also declare that the intellectual content of this thesis is the product of my own work, except to the extent that assistance from others in the project's design and conception or in style, presentation and linguistic expression is acknowledged.'

Signed

Date

COPYRIGHT STATEMENT

I hereby grant the University of New South Wales or its agents the right to archive and to make available my thesis or dissertation in whole or part in the University libraries in all forms of media, now or here after known, subject to the provisions of the Copyright Act 1968. I retain all proprietary rights, such as patent rights. I also retain the right to use in future works (such as articles or books) all or part of this thesis or dissertation.

I also authorise University Microfilms to use the 350 word abstract of my thesis in Dissertation Abstract International (this is applicable to doctoral theses only).

I have either used no substantial portions of copyright material in my thesis or I have obtained permission to use copyright material; where permission has not been granted I have applied/will apply for a partial restriction of the digital copy of my thesis or dissertation.'

Signed

Date

AUTHENTICITY STATEMENT

'I certify that the Library deposit digital copy is a direct equivalent of the final officially approved version of my thesis. No emendation of content has occurred and if there are any minor variations in formatting, they are the result of the conversion to digital format.'

Signed

Date

PLEASE TYPE**THE UNIVERSITY OF NEW SOUTH WALES
Thesis/Dissertation Sheet**

Surname or Family name: Guo

First name: Rui

Other name/s:

Abbreviation for degree as given in the University calendar: M Eng

School: School of Materials Science and Engineering

Faculty: Faculty of Science

Title: Thermophysical properties and radiation tolerance of
NdCrO₃ and NdAlO₃**Abstract 350 words maximum: (PLEASE TYPE)**

Nuclear power is a popular and sustainable method to generate electricity. In order to increase the economic efficiency, it is possible to add dopants into nuclear fuel to increase the fuel burn-up. PuCrO₃ and PuAlO₃ have been demonstrated to be formed in UO₂ fuel because of the interaction of additives (Cr₂O₃ and Al₂O₃) and Pu that is produced by neutron capture reactions. The formation of these phases will have impact on the properties of the waste form generated from the spent fuel. Here, the thermo-physical properties and radiation tolerance of these chromates and aluminates have been examined using Nd as a surrogate for Pu.

In this project, two kinds of perovskite-type ceramic materials (NdCrO₃ and NdAlO₃) were investigated to simulate PuCrO₃ and PuAlO₃. They were prepared using co-precipitation followed by cold isostatic or uniaxial pressing and conventional sintering. Thereafter, heat capacity, thermal expansion and thermal diffusivity were measured to calculate the thermal conductivity of neodymium chromate and neodymium aluminate. Neodymium aluminate showed higher thermal conductivity than that of neodymium chromate. Ion beam irradiation using Au-ions and He-ions has been utilized to simulate the consequences of α -decay and the effects of irradiation on the structural and macroscopic properties have been investigated. Irradiation by Au-ions resulted in volume swelling, a loss in long-range order, a reduction in hardness for neodymium aluminate and an increase in hardness for neodymium chromate at fluences above 10¹⁴ Au-ions/cm². On the contrary, little effect on the materials properties was observed for samples irradiated with He-ions up to a fluence of 10¹⁷ ions/cm².

In summary, the thermal conductivity of neodymium chromate and neodymium aluminate were investigated. The radiation tolerance of these two kinds of ceramic materials were also studied. The results indicated that the presence of plutonium chromate and plutonium aluminate may have significant impact on the properties of spent uranium dioxide fuel.

Declaration relating to disposition of project thesis/dissertation

I hereby grant to the University of New South Wales or its agents the right to archive and to make available my thesis or dissertation in whole or in part in the University libraries in all forms of media, now or here after known, subject to the provisions of the Copyright Act 1968. I retain all property rights, such as patent rights. I also retain the right to use in future works (such as articles or books) all or part of this thesis or dissertation.

I also authorise University Microfilms to use the 350 word abstract of my thesis in Dissertation Abstracts International (this is applicable to doctoral theses only).

.....
Signature.....
Witness.....
Date

The University recognises that there may be exceptional circumstances requiring restrictions on copying or conditions on use. Requests for restriction for a period of up to 2 years must be made in writing. Requests for a longer period of restriction may be considered in exceptional circumstances and require the approval of the Dean of Graduate Research.

FOR OFFICE USE ONLY

Date of completion of requirements for Award:

THIS SHEET IS TO BE GLUED TO THE INSIDE FRONT COVER OF THE THESIS

Acknowledgement

Thank you to the University of New South Wales School of Material Sciences and Engineering for providing the opportunity for research on this project. I have been indebted in the preparation of my thesis to my supervisor, Professor Sean Li and co-supervisor, Dr Dan Gregg, whose patience and kindness as well as academic experience and knowledge have been invaluable to me.

Abstract

Nuclear power is a popular and sustainable method to generate electricity. In order to increase the economic efficiency, it is possible to add dopants into nuclear fuel to increase the fuel burn-up. PuCrO_3 and PuAlO_3 have been demonstrated to be formed in UO_2 fuel because of the interaction of additives (Cr_2O_3 and Al_2O_3) and Pu that is produced by neutron capture reactions. The formation of these phases will have impact on the properties of the waste form generated from the used fuel. Here, the thermophysical properties and radiation tolerance of these chromates and aluminates have been examined using Nd as a surrogate for Pu.

In this project, two kinds of perovskite-type ceramic materials (NdCrO_3 and NdAlO_3) were investigated to simulate PuCrO_3 and PuAlO_3 . They were prepared using co-precipitation followed by cold isostatic or uniaxial pressing and conventional sintering. Thereafter, heat capacity, thermal expansion and thermal diffusivity were measured to calculate the thermal conductivity of neodymium chromate and neodymium aluminate. Neodymium aluminate showed higher thermal conductivity than that of neodymium chromate. Ion beam irradiation using Au-ions and He-ions has been utilized to simulate the consequences of α -decay and the effects of irradiation on the structural and macroscopic properties have been investigated. Irradiation by Au-ions resulted in volume swelling, a loss in long-range order, a reduction in hardness for neodymium aluminate and an increase in hardness for neodymium chromate at fluences above 10^{14} Au-ions/cm². On the contrary, little effect on the materials properties was observed for samples irradiated with He-ions up to a fluence of 10^{17} ions/cm².

In summary, the thermal conductivity of neodymium chromate and neodymium aluminate were investigated. The radiation tolerance of these two kinds of ceramic materials were also studied. The results indicated that the presence of plutonium chromate and plutonium aluminate may have significant impact on the properties of used uranium dioxide fuel.

Table of Contents

Acknowledgement	i
Abstract.....	ii
Table of Contents	iv
List of Figures	vii
Chapter 1 Introduction	1
Chapter 2 Literature Review	5
2.1 Introduction.....	5
2.2 Thermal conductivity	6
2.2.1 Theory of thermal conductivity.....	6
2.2.2 Influencing factors of thermal conductivity	9
2.3 Synroc (Synthetic Rock)	10
2.4 Radiation damage.....	12
2.4.1 Radiation damage theory	12
2.4.2 Property degradation phenomena induced by the radiation	14
2.4.3 Radiation-induced effects on ceramic materials properties	16
2.4.4 Radiation damage using ion beam	18
2.5 Perovskite structure.....	20
2.5.1 Structure of NdCrO_3 & NdAlO_3	22
2.6 Previous work on PuAlO_3 & PuCrO_3	24
2.6.1 Structure of PuAlO_3 & PuCrO_3	24
2.6.2 Thermal stability of PuCrO_3 and PuAlO_3	26
2.6.3 Thermal conductivity of PuCrO_3 and PuAlO_3	26
2.7 Summary	28
Chapter 3 Experimental	29
3.1 Introduction.....	29
3.2 Sample preparation	29
3.3 Thermo-physical analysis	34

3.3.1	Specific heat capacity.....	35
3.3.2	Thermal expansion.....	35
3.3.3	Thermal diffusivity	36
3.4	Characterization	37
3.4.1	X-ray diffraction	38
3.4.2	Grazing Incidence X-ray Diffraction	39
3.4.3	Scanning Electron Microscopy (SEM)	40
3.4.4	Raman Spectroscopy.....	41
3.4.5	Nano-indentation.....	43
3.4.6	Thermal annealing.....	44
3.5	Ion beam irradiation.....	45
Chapter 4	Characterization of pristine NdCrO ₃ and NdAlO ₃	49
4.1	Introduction.....	49
4.2	Results and discussion	50
4.2.1	X-ray diffraction	50
4.2.2	Scanning electron microscopy (SEM)	51
4.2.3	Density measurement.....	53
4.2.4	Raman analysis	53
4.3	Conclusion	55
Chapter 5	Thermophysical Properties of NdCrO ₃ and NdAlO ₃	57
5.1	Introduction.....	57
5.2	Results and Discussion.....	58
5.2.1	Heat Capacity(C _p)	58
5.2.2	Thermal expansion.....	59
5.2.3	Thermal diffusivity	60
5.2.4	Thermal conductivity	61
5.3	Conclusions.....	65
Chapter 6		66
Ion beam irradiation and Characterization on irradiated NdCrO ₃ & NdAlO ₃		66

6.1	Introduction.....	66
6.2	Results and Discussions	66
6.2.1	Grazing incidence X-ray diffraction	66
6.2.2	Cross-sectional SEM.....	73
6.2.3	Cross-sectional Raman analyses	80
6.2.4	Hardness Measurements	92
6.2.5	Thermal annealing after ion irradiation.....	99
6.3	Conclusions.....	103
Chapter 7 Conclusion.....		105
References.....		109

List of Figures

Figure 1. Synroc waste form [30]	12
Figure 2. Schematic of compositions of example perovskite structures.	21
Figure 3. Cubic perovskite unit cell. Blue spheres represent the A cations, yellow spheres represent the B cations, and red spheres represent oxygen anions forming an octahedral [45]..	22
Figure 4. Pnma, orthorhombic perovskite cell. Blue spheres represent the A cations, yellow spheres represent the B cations, and red spheres represent oxygen anions forming an octahedral [45].....	23
Figure 5. R-3c rhombohedral perovskite unit cell. Blue spheres represent the A cations, yellow spheres represent B cations, and red spheres represent oxygen [45]	23
Figure 6. The predicted lowest energy structure of PuCrO ₃ – the Pnma orthorhombic structure (i) illustrates the structure viewed down the z-axis, highlighting the Cr–O octahedral distortions (red polyhedra) around the Pu ions (blue).	25
Figure 7. variation of thermal conductivity with temperature of stoichiometric UO ₂ , PuCrO ₃ and PuAlO ₃ (both rhombohedral and orthorhombic lattices) [6].....	27
Figure 8. XRD pattern of CIPed NdCrO ₃ and no- CIPed NdCrO ₃ that sintered to 1600°C.	33
Figure 9. XRD patterns of CIPed NdAlO ₃ and no- CIPed NdAlO ₃ that sintered to 1600°C.....	34
Figure 10. Diagram of heating pattern and system geometry (R=reference S=sample).....	35
Figure 11. Schematic illustration of the pushrod dilatometer.	36
Figure 12. Schematic illustration of the sample chamber in LFA 467.	37
Figure 13. Schematic illustration of the Bragg’s law.....	38
Figure 14. Schematic illustration of the symmetric GI-XRD geometry.	39
Figure 15. Schematic diagram of the principle of SEM.....	41
Figure 16. Energy level diagram showing the states involved in Raman level.	43
Figure 17. Schematic illustration of Nano-indentation measurement.....	44
Figure 18. Australia National Tandem Research (ANTARES) Accelerator [69].....	47

Figure 19. Displacement per atom as a function of irradiation depth of NdCrO ₃ for Au or He ions calculated using SRIM 2013.	48
Figure 20. Displacement per atom as a function of irradiation depth of NdAlO ₃ for Au or He ions calculated using SRIM 2013.	48
Figure 21. Indexed X-ray diffraction pattern of NdCrO ₃ , with standard patterns for PuCrO ₃ and NdCrO ₃ shown below.	51
Figure 22. Indexed X-ray diffraction pattern of NdAlO ₃ , with standard patterns for PuAlO ₃ and NdAlO ₃ shown below.	51
Figure 23. Scanning electron micrograph of NdCrO ₃ sintered for 26h at 1600°C with 500 X and 1000 X magnification. The black areas are pores.	52
Figure 24. Scanning electron micrograph of NdAlO ₃ sintered for 26h at 1600°C with 200 X and 500 X magnification. The black areas are pores and cracks.	52
Figure 25. Raman spectra for polished pristine NdCrO ₃ and NdAlO ₃ samples.	55
Figure 26. Temperature dependence of heat capacity of NdAlO ₃ and NdCrO ₃ heating to 1100°C.	58
Figure 27. Temperature dependency of thermal expansion of NdCrO ₃ and NdAlO ₃ heating to 1100°C.	59
Figure 28. Temperature dependence of thermal diffusivity of NdCrO ₃ and NdAlO ₃ heating to 1100°C.	60
Figure 29. Temperature dependence of thermal conductivity of NdCrO ₃ and NdAlO ₃	62
Figure 30. GI-XRD pattern using a 5° incidence angle for (—) un-irradiated, (— —) 10 ¹³ , (—·) 10 ¹⁴ and (··)10 ¹⁵ Au-ions/cm ² irradiated NdCrO ₃	67
Figure 31. Variation of crystallinity of NdCrO ₃ versus ion fluence.	68
Figure 32. Unit cell volume variation versus ion fluence in NdCrO ₃ irradiated with Au ions. ...	70
Figure 33. GI-XRD pattern using a 5° incidence angle for (—) un-irradiated, (— —) 10 ¹³ , (—·) 10 ¹⁴ and (··)10 ¹⁵ Au-ions/cm ² irradiated NdAlO ₃	72
Figure 34. Variation of crystallinity of NdAlO ₃ versus ion fluence.	72

Figure 35. Unit cell volume variation versus ion fluence in NdCrO ₃ irradiated with Au ions. ...	73
Figure 36. Crystallographic contrast observed following SEM analysis of the cross-sectioned NdCrO ₃ pellet irradiated with Au-ions at the fluence of 10 ¹³ ions/cm ²	74
Figure 37. Crystallographic contrast observed following SEM analysis of the cross-sectioned NdCrO ₃ pellet irradiated with Au-ions at the fluence of 10 ¹⁴ ions/cm ²	74
Figure 38. Crystallographic contrast observed following SEM analysis of the cross-sectioned of the NdCrO ₃ pellet irradiated with Au-ions at the fluence of 10 ¹⁵ ions/cm ²	75
Figure 39. Crystallographic contrast observed following SEM analysis of the cross-sectioned of the NdAlO ₃ pellet irradiated with Au-ions at the fluence of 10 ¹³ ions/cm ²	76
Figure 40. Crystallographic contrast observed following SEM analysis of the cross-sectioned of the NdAlO ₃ pellet irradiated with Au-ions at the fluence of 10 ¹⁴ ions/cm ²	77
Figure 41. Crystallographic contrast observed following SEM analysis of the cross-sectioned of the NdAlO ₃ pellet irradiated with Au-ions at the fluence of 10 ¹⁵ ions/cm ²	77
Figure 42. Crystallographic contrast observed following SEM analysis of the cross-sectioned NdCrO ₃ pellet irradiated with He-ions at the fluence of 10 ¹⁶ ions/cm ²	79
Figure 43. Crystallographic contrast observed following SEM analysis of the cross-sectioned NdCrO ₃ pellet irradiated with He-ions at the fluence of 10 ¹⁷ ions/cm ²	79
Figure 44. Crystallographic contrast observed following SEM analysis of the cross-sectioned NdAlO ₃ pellet irradiated with He-ions at the fluence of 10 ¹⁶ ions/cm ²	80
Figure 45. Crystallographic contrast observed following SEM analysis of the cross-sectioned NdAlO ₃ pellet irradiated with He-ions at the fluence of 10 ¹⁷ ions/cm ²	80
Figure 46. Raman spectra on cross-sectioned NdCrO ₃ following 10 ¹⁵ Au-ions/cm ² irradiation.	82
Figure 47. Raman micro-spectrometry spectra of sectioned pellets of pristine and Au-ion irradiated NdCrO ₃	82
Figure 48. Raman spectra on cross-sectioned NdAlO ₃ irradiated with 10 ¹⁵ Au-ions/cm ²	85
Figure 49. Raman microspectrometry spectra of sectioned pellets of pristine and Au-ion irradiated NdAlO ₃	85

Figure 50. Raman spectra on NdCrO ₃ following 10 ¹⁷ He-ions/cm ² irradiation.	88
Figure 51. Raman microspectrometry spectra of sectioned pellets of pristine and 10 ¹⁷ He ions/cm ² irradiated NdCrO ₃ taken at a depth of 18 μm.	89
Figure 52. Raman spectra of NdAlO ₃ following 10 ¹⁷ He-ions/cm ² irradiation.	90
Figure 53. Raman microspectrometry spectra of sectioned pellets of pristine and He ion irradiated NdAlO ₃ . Spectra were taken at a depth of 12 μm.	91
Figure 54. Load on sample versus displacement in un-irradiated NdAlO ₃	92
Figure 55. Hardness variation versus displacement in un-irradiated NdAlO ₃	93
Figure 56. Load on sample versus displacement in NdAlO ₃ irradiated with 10 ¹⁵ Au-ions/cm ²	93
Figure 57. Hardness variation versus displacement in NdAlO ₃ irradiated with 10 ¹⁵ Au-ions/cm ²	94
Figure 58. Load on sample versus displacement in un-irradiated NdCrO ₃	95
Figure 59. Hardness variation versus displacement in un-irradiated NdCrO ₃	95
Figure 60. Load on sample versus displacement in NdCrO ₃ irradiated with 10 ¹⁵ Au-ions/cm ²	96
Figure 61. Hardness variation versus displacement in NdCrO ₃ irradiated with 10 ¹⁵ Au-ions/cm ²	96
Figure 62. Temperature evolution of the GI-XRD data using a 2° incidence angle for NdCrO ₃ with a fluence of 10 ¹⁵ Au-ions/cm ² . Samples are annealed for 2h at the designated temperature and then measured before further annealing at higher temperature. Patterns are plotted as diffraction intensity vs angle (° 2θ). Main peaks in the pattern are for NdCrO ₃ , and # indicate neodymium oxide, * indicate chromium oxide.	100
Figure 63. Temperature evolution of the GI-XRD data using a 2° incidence angle for NdAlO ₃ with a fluence of 10 ¹⁵ Au-ions/cm ² . Samples are annealed for 2h at the designated temperature and then measured before further annealing at higher temperature. Patterns are plotted as diffraction intensity vs angle (°2θ). Main peaks in the pattern are for NdAlO ₃ , # indicate neodymium oxide and * indicate alumina.	101

List of Tables

Table 1 Ceramic Power Synthesis approaches [51].	30
Table 2. The list of different sintering temperature for CIPed and no CIPed NdCrO ₃ and NdAlO ₃ .	33
Table 3. Energy fraction (f_{elec} and f_{nucl}), depth profile and the main characteristics for irradiated NdCrO ₃ and NdAlO ₃ based on SRIM 2013	47
Table 4. Bulk density measured with Archimedes' Principle and theoretical density of NdCrO ₃ and NdAlO ₃ .	53
Table 5. Comparison of specific heat capacity, thermal expansion and thermal diffusivity among NdCrO ₃ , NdAlO ₃ and UO ₂ (from literature) [80, 81]	61
Table 6. Thermal conductivities of different samples at the temperatures of 400 and 1100 °C. Data of PuCrO ₃ , PuAlO ₃ and UO ₂ through computational method is from literature by Fullarton, data of UO ₂ through experimental result is from literature by Pillai [82].	63
Table 7 Lattice parameter and unit cell volume of un-irradiated, 10 ¹³ , 10 ¹⁴ and 10 ¹⁵ Au ions/cm ² irradiated NdCrO ₃	70
Table 8 Lattice parameter and unit cell volume of un-irradiated, 10 ¹³ , 10 ¹⁴ and 10 ¹⁵ Au ions/cm ² irradiated NdAlO ₃	73
Table 9. Average hardness of pristine and 10 ¹⁵ Au-ions/cm ² irradiated NdCrO ₃ and NdAlO ₃ .	97
Table 10. Standard deviation of average hardness of pristine and 10 ¹⁵ Au-ions/cm ² irradiated NdCrO ₃ and NdAlO ₃ .	97

Chapter 1 Introduction

Nuclear power is a popular and sustainable method used to produce heat. In recent years, the generated heat usually is then used to produce electricity and the nuclear power has become one of the main power to provide the world's electricity [1]. The reason for its popularity is that the same as other sustainable power sources, nuclear fission power is a low carbon power generation method of producing electricity [2].

With the worldwide use of nuclear power to generate electricity, it is inevitable that radioactive waste as a by-product of nuclear power generation will be produced. The radioactive waste contains radioactive material which is harmful to human beings and the environment. Used fuel is the most important waste from nuclear power plants; and consists of un-converted uranium and some transuranic actinides such as plutonium and curium [3]. The radioactive waste can be classified as uranium tailings, low-level waste, intermediate-level waste and high-level waste. Depending on the classification, these wastes must be stored separately and confined in appropriate disposal facilities. Specifically, low and some intermediate level waste are managed by near-surface disposal and deep burial is the management for the high-level waste [4]. Aside from these management methods for radioactive waste, reprocessing is necessary to reduce uranium and plutonium that remain in long-term radioactive waste as it can probably recover significant amounts of uranium and plutonium in used nuclear fuel and then can be used in new mixed oxide fuel.

For many years, the increase of efficiency in the production of nuclear electricity has been an economic challenge in many countries. Therefore, the increase of fuel burn up

has been put forward as it can cause a reduction in the volume of used fuel discharged to longer fuel cycles in the reactor, which means bigger availability and capacity factors [5]. In other words, in the nuclear field as well as in many other fields, it is always vital and economical to improve performance. In order to increase the fuel burn-up, it is possible to extract more power from nuclear fuel and therefore increase the economic efficiency [6].

Recently, based on this aim, there has considerable research focused on UO_2 fuels; some dopants can be added to improve the in-reactor behaviour of fuels. The additives include Cr_2O_3 , Al_2O_3 and SiO_2 . With these dopants adding into the UO_2 fuel, the fuel microstructure can be altered. In addition, these dopants are likely to interact with the fission products that form in-reactor [6]. According to Russel [7], it has been confirmed that PuCrO_3 and PuAlO_3 can be formed in the UO_2 fuel. This is because two common UO_2 fuel dopants (Cr_2O_3 and Al_2O_3) can interact with Pu that is generated by neutron capture reactions with U-238 in UO_2 fuel. Therefore, because of the formation of PuCrO_3 and PuAlO_3 , they may decompose or form phases which may leach out of the used fuel if it were to be sent to a waste repository. If they are not radiation tolerant, this may enhance the leaching of plutonium from used fuel which is currently considered as a waste form in some countries.

Hence, in this project, it is important to understand the thermal properties and radiation tolerance of PuCrO_3 and PuAlO_3 . As PuCrO_3 and PuAlO_3 are radioactive materials, Nd is chosen as a non-radioactive surrogate for Pu. The reason for choosing Nd as a substitution is because of their ionic radii and oxidation state similarity. In terms of ionic radii, Nd^{3+} and Pu^{3+} have similar ionic radii that are 1.123 and 1.14, respectively [8], which means they can substitute into ionic crystal structures similarly. As for

oxidation states, they have the same oxidation states. In UO_2 fuel, Pu is a trivalent cation which is the same as Nd. Also, as a surrogate, density is another factor to consider particularly as density will influence the thermal properties. However, as the density during operation is expected to vary considerably. I targeted materials with high density in order to facilitate characterisation. In this project, the measurement of thermal properties and ion beam irradiation will be applied on NdCrO_3 and NdAlO_3 and the conclusion can then be made with the results of measurements and characterizations.

In this thesis, two perovskite-type materials, NdCrO_3 and NdAlO_3 were studied. In Chapter 2, the important thermo-physical properties, which include specific heat capacity, thermal expansion and thermal diffusivity, were explained. The general introduction of synroc, ion beam irradiation and perovskite structure was summarized. In addition, the previous researches on neodymium chromate and neodymium aluminate were reviewed. In Chapter 3, in order to synthesise neodymium chromate and neodymium aluminate ceramics, some powder preparation methods were introduced generally. The conventional sintering process was introduced for the ceramic preparation. The measurement methods, main characterizations and ion beam irradiation utilized in this project have been described briefly. In Chapter 4, several characterizations on as-prepared neodymium chromate and neodymium aluminate were described. These basic characterizations were important to establish the purity, crystallinity and density of these ceramics. In Chapter 5, specific heat capacity, thermal expansion and thermal diffusivity of neodymium chromate and neodymium aluminate were measured to calculate the thermal conductivity. In Chapter 6, several characterizations on Au and He-ion irradiated neodymium chromate and neodymium aluminate were described. Following this, thermal annealing for irradiated materials was employed to investigate the recrystallization condition. In the last chapter, the

conclusions were made on the thermophysical properties and radiation tolerance of these two materials. The main contribution of this project was concluded.

Chapter 2 Literature Review

2.1 Introduction

PuCrO_3 and PuAlO_3 are compounds likely formed in UO_2 fuel following reaction of Cr_2O_3 and Al_2O_3 with Pu. Their formation may have some impact on the used fuel when stored as waste for a long time. Therefore, it is necessary to investigate the thermophysical properties and radiation tolerance of PuCrO_3 and PuAlO_3 . In this work, Neodymium is used as a surrogate for plutonium. It is important to have a deep understanding of thermophysical properties, radiation damage and previous research on PuCrO_3 and PuAlO_3 . Meanwhile, Synroc, a safe method of storing nuclear radioactive waste was reviewed.

Thermophysical properties can be explained as material properties that vary with temperature without changing the chemical identity of material. To be specific, thermophysical properties are the material properties that can affect the heat storage and transfer. It varies with the state variables like temperature, pressure and composition and of other factors. These properties include specific heat capacity, thermal expansion, thermal diffusivity as well as viscosity and thermal diffusion coefficients. In this project, thermal conductivity (specific heat capacity, thermal expansion and thermal diffusivity) was investigated.

According to Konings [9], it is more than a century ago that radiation effects on the structure and properties of materials were first being studied, and since 1940s, the focus on it had increased because of the development of fission reactors. From 1950s to early 1960s, the crystalline defects were studied productively. In the 1960s and 1970s, as the study of radiation damage processes in materials, heavy ion irradiation was focused on

study; recently, ion beam irradiation has become a significant application to simulate radiation damage. The popularity of ion beam irradiation is due to the ability to investigate basic processes with enormous time- and money-saving. As for ceramics, there are types of ceramics that are highly robust ceramics, which can withstand high radiation doses. PuCrO_3 and PuAlO_3 that can be formed in UO_2 fuel are perovskite-type ceramics.

This chapter is an introduction into thermal conductivity, synroc, ion beam irradiation and radiation effects on ceramics. The perovskite structure is also introduced to provide a basic understanding of the PuCrO_3 and PuAlO_3 structures. Meanwhile, in order to have a deep understanding on these two materials and this project, previous work was summarized in this chapter as well.

2.2 Thermal conductivity

2.2.1 Theory of thermal conductivity

Thermal conductivity (K) is a kind of material's property to conduct heat. It is defined as under unit temperature difference and unit time, the heat conducted directly by the unit section and the length of the material. It illustrates the heat transport through a body of mass as the result of a temperature gradient. In a material, thermal conductivity can be divided into two sources: electronic (K_e) and the lattice (K_L) [10, 11].

$$\kappa = \kappa_e + \kappa_L \quad (1)$$

- **Electronic thermal conductivity**

The electronic thermal conductivity(κ_e) could be described by the Wiedemann-Franz law [12]:

$$\kappa_e = L\sigma T \quad (2)$$

Where L is the Lorenz number ($2.44 \times 10^{-8} \text{W}\Omega\text{K}^{-2}$) [13], σ is the electrical conductivity and T is the temperature.

Therefore, a material with a high electrical conductivity will have a high electronic thermal conductivity. Namely, it will have a higher total thermal conductivity and the thermal properties of a material are interdependent.

▪ **Lattice thermal conductivity**

In terms of the lattice thermal conductivity (κ_L), it can be described by the lattice vibrations (phonons) and is independent of electronic properties.

At First, Debye [14] and Peierls [15] put forward the early theories of the lattice conductivity, λ_g . After that, with several authors' effort on working out refined theories, an exact calculation of λ_g perfect crystals is feasible in principle and it focuses on two aspects: on the phonon spectrum as well as on the anharmonicity of the lattice forces of a material. Equation 4 below describes lattice thermal conductivity (κ_L).

$$\kappa_L = \frac{1}{3} C_v v l = \frac{1}{3} C_v v^2 \tau \left(v = \frac{l}{\tau} \right) \quad (3)$$

Where C_v is the heat capacity, v is the phonon velocity and l is the phonon mean free path and lattice thermal conductivity is the product of these parameters.

The phonon mean free path (l) is the product of the phonon velocity (v) and the phonon relaxation time τ . The phonon velocity (v) always approximates the low frequency of

the sound speed ($v_s \propto \sqrt{B/\delta}$) in which B stands for the elastic modulus and δ is the material's density [16-20]. Generally, sound velocity and the phonon mean free path are the two parameters that can determine the lattice thermal conductivity. A low sound velocity and the small phonon mean free path can dominate the low lattice thermal conductivity and therefore causes low thermal conductivity.

- **Debye model for Specific heat**

The Debye model was first developed by Peter Debye in 1912. Vibrational motion of atoms is the considered factor that can decide the heat capacity. It is used to estimate the phonon contribution to the heat capacity in a solid [21] and treats the vibrations of the atomic lattice as phonons in a box. The Debye temperature (θ_D) is the most important parameter to predict the specific heat capacity and it is defined by [22]:

$$\theta_D = \frac{hw_D}{K_B} \quad (4)$$

Where K_B is the Boltzmann's constant, h is Plank's constant and W_D is the maximum frequency of the vibrations of a solid's atoms.

The Debye model predicts that the low temperature is related to the heat capacity. It means when the temperature $T \leq \theta_D$, it is proportional to T^3 - the Debye T^3 law. When the temperature $T \geq \theta_D$, it agrees with Dulong-Petit law. However, it is not accurate at intermediate temperatures because of the simplifying assumptions [23].

2.2.2 Influencing factors of thermal conductivity

The thermal conductivity cannot keep constant all the time, and there are several factors that can affect the thermal conductivity. These factors include the inner structure of material, the density of material, moisture of material, ambient temperature, chemical phase and so on. With the change of density, moisture and temperature, the thermal conductivity alters as well.

- **Temperature**

There are some differences between metals and non-metals in terms of the effect on temperature on thermal conductivity. For metals, the conductivity is due to free electrons. Namely, the conductivity always tracks the electrical conductivity as the free electrons in metals transfer both electric current and the heat energy and it is about proportional to the absolute temperature multiplied by electrical conductivity. In pure metals, with the increase of the temperature, the electrical conductivity decreases. Thus, the thermal conductivity, which is the product of the electrical conductivity and the temperature, will remain almost constant. However, in alloys, as the change in temperature is always more obvious than that of electrical conductivity, the thermal conductivity is dependent on the temperature, and it will increase with the temperature.

On the contrary, in non-metals, the lattice vibrations (phonons) dominate the heat conductivity but this is not suitable for high quality crystals at low temperature. Hence, the thermal conductivity for non-metals will vary with varied temperatures: at high temperatures, the thermal conductivity will almost stay the same; however, when the temperature is low which is below the Debye temperature, both thermal conductivity and the heat capacity decrease [24].

- **Chemical phase of material**

The type of material used in thermal conductivity can affect the rate of energy flowing between the two regions, and the energy flow is proportional to the conductivity of the material. In a material, the thermal conductivity may change with a phase change from solid to liquid or from liquid to gas and liquids and gas have lower thermal conductivity than that of solid. For example, when ice melts and becomes liquid water, the thermal conductivity would change from 2.18 W/ (mK) to 0.56 W/ (mK) at the same temperature (0°C) [25].

- **Thermal anisotropy**

In some materials, the thermal conductivity can be different due to the various crystal axes. This is because of the differences in phonon coupling along a given crystal axis. Take sapphire as a markedly example, the thermal conductivity of sapphire is determined by the orientation and temperature; therefore, the thermal conductivity can vary from 35 W/(mK) with c axis to 32 W/(mK) with a axis [26].

2.3 Synroc (Synthetic Rock)

As for nuclear radioactive waste disposal, there are many management methods such as vitrification, ion exchange, geologic disposal, above-ground disposal. Unlike these traditional methods that degrade over time, synroc is a set of technologies that provide the most effective and durable means to immobilise different levels of radioactive wastes for disposal. Synroc tailored waste forms are built on minerals that have withstood weathering process in nature for 100's of millions of years [27].

Synroc, an abbreviation of “synthetic rock”, is a method of safely storing radioactive waste. It was first invented in 1978 at the Australian National University and ANSTO does further research on it. Synroc is a kind of ceramic that is constituted of stable natural titanate minerals, and it has been utilized to immobilise uranium and thorium for billions of years. Specifically, the natural titanate minerals can be mixed with these high-level radioactive waste and incorporate into their crystal structures and therefore immobilise them. The main titanate minerals contain hollandite ($\text{BaAl}_2\text{Ti}_6\text{O}_{16}$), zirconolite ($\text{CaZrTi}_2\text{O}_7$) and perovskite (CaTiO_3). Among these three types of minerals, zirconolite and perovskite are the hosts of long-lived actinides like plutonium (Pu), strontium (Sr) and barium (Ba). Hollandite usually is the host of caesium (Cs) and barium (Ba) [27, 28].

As for the working process of synroc, there are several steps. First, the radioactive waste is mixed with tailored rock-forming additives; the mixture is then heated. Thereafter, canisters are filled with the mixture and then be sealed. The canister is placed inside a hot isostatic press (HIP) and argon is pumped into the vessel. Next, the canister is heated and is applied with moderate pressure. In this case, the powdered mixture fuses together to form solid block, the result is a cylinder of hard, dense and black synthetic rock (**Figure 1**), and the radioactive waste is locked up into the molecular lattice of the waste form. Due to its specific design, the canister collapses to form a cylindrical shape to store the radioactive waste more efficiently [29]. The reason for utilizing HIP technology is its key advantages: lower emissions, higher waste loadings and very flexible technology.

Overall, if nuclear waste stored in a liquid form, the waste can be hazardous to the environment and the waterways and therefore can induce extensive damage to the

environment and human. By contrary, when nuclear waste stored as synroc waste form which is held in a solid lattice, chances of the waste elements spreading are greatly reduced.



Figure 1. Synroc waste form [30]

2.4 Radiation damage

Radiation damage is the damage done to the crystal lattice. When ion beam irradiation is utilized for radiation damage study, radiation effects study can be carried out using various kinds of energetic particles including neutrons, electrons, protons, He ions and heavy ions and this can be conducted using the ion beam accelerator.

2.4.1 Radiation damage theory

The interaction of energetic particles with a solid target is a complex process. The primary damage produced in collision events is the energetic particles interact with a solid target and create primary knock-on atoms by scattering accelerated ions [9]. Norgett et al. [31] generated a model that known as the Norgett-Robinsion-Torrens (NRT) standard and this is the model that is used to predict the number of displacements created by a primary knock-on atoms carrying potential part of the kinetic energy

(Epka). The Norgett-Robinson-Torrens model is governed by the following equation [32, 33].

$$N_d(T_d) = \begin{cases} 0 & T_d < E_d \\ 1 & E_d \leq T_d < \frac{2E_d}{\beta} \\ \beta T_d / 2E_d & \frac{2E_d}{\beta} \leq T_d < \infty \end{cases} \quad (5)$$

Where E_d is the effective threshold displacement energy, β is the scattering correction factor. T_d in this expression is the damage energy.

This theory is based on the hypothesis that in order to be displaced from its lattice site, a minimum amount of energy should be provided for a primary knock-on atom to strike a lattice atom. When the energy received for collision in the lattice atom is less than the threshold displacement energy (E_d), the knocked atom undergoes vibrations but still remains in its lattice site. Thereafter, part of the kinetic energy (E_{PKA}), transmitted to the primary knock-on atoms (PKA) is lost to the electron excitation. Then, the rest of the energy, which is called the damage energy (T_d), is dissipated in elastic collisions between atoms. In addition, if the damage energy (T_d) exceeds threshold displacement energy (E_d), the vacancy-interstitial (Frenkel) pairs are produced for the target material [9, 33].

One of the consequences of the interaction of energy particles (ions, photons or electrons) with crystalline materials is the formation of lattice defects as the energy transfers to the atoms. This consequence is the reason that can explain why radiation has both harmful and good effects on materials. The damage can show different forms: in a crystal, an atom can be kicked out from its initial lattice site, this will lead to a vacancy and create an atom at an interstitial site in front [32]. Defects can be formed after radiation damage and can be defect clusters, amorphous zones or dislocation loops.

The radiation damage can be divided into two types: the primary damage which is formed immediately after the energy particles like ions impact by collision processes, and the long-time scale damage evolution caused by thermally activated processes [32]. The damage (primary damage or damage evolution with time) can induce macroscopic response of a material to radiation and the property degradation phenomena induced by the radiation is introduced below.

2.4.2 Property degradation phenomena induced by the radiation

With energetic particles irradiated on materials, atomic displacements can be created and significant microstructural alteration can be induced. These microstructural changes can always cause alterations in the physical and mechanical properties on the irradiated materials.

Materials undergo radiation will experience the alteration on the microstructure and the macroscopic, mechanical properties of the materials and some major phenomena may occur in irradiated materials. These changes include radiation hardening, radiation-induced amorphization, thermal and electrical conductivity degradation, corrosion degradation, dimensional instabilities and high temperature embrittlement, and they are summarized below.

Radiation induced amorphization can be found in ceramics, metals and alloys. According to Weber et al. [34], the phase transition from crystalline to amorphous can be induced at very low temperatures when the motion of self-interstitial atoms is limited. During the phase transition, there will be other changes produced such as large swelling and decreases in elastic module in materials.

Radiation induced hardening is another degradation phenomenon that occurs in metals and alloys. The reason for materials get hardening after irradiation is due to the creation of high densities of impenetrable clusters, which act as obstacles to dislocation motion. These obstacles also include point defects, small clusters and precipitates. Usually, radiation hardening in metals and alloys will result in some consequences; for instance, materials will show increased strength, decreased tensile elongation and reduction in toughness and some of these consequences may be beneficial to materials but others may have detrimental impacts on materials.

It is common that thermal and electrical conductivity will decrease after radiation and this can occur over a wide range of irradiation temperatures [9]. For non-metallic irradiated materials, the thermal conductivity decreases by displacement damage because of phonon scattering by point defects and defect clusters. While for metals, the reasons for causing the decrease of thermal conductivity are due to the electron scattering from point defects and nuclear transmutation of solute atoms.

Besides these degradation phenomena, there are some other effects induced by radiation. Radiation induced segregation and precipitation, which can occur when self-interstitial atoms and vacancies are mobile at intermediate temperatures; the dimensional instabilities (irradiation growth, creep and swelling), which can occur due to the anisotropic nucleation and growth of dislocation loops, the presence of applied stress and void formation; and the high temperature embrittlement which always occurs at high temperature [9].

2.4.3 Radiation-induced effects on ceramic materials properties

It is apparent that radiation can induce alterations in the physical properties of ceramics. In order to understand the effects on ceramics after irradiation, there were many previous works done on several types of ceramic materials. Based on the results of radiation damage in different kinds of ceramic materials, after irradiation, materials show the amorphization, mechanical and thermal property alteration.

According to Hobbs et al [35-37], when they did research on the ceramic materials like ZrSiO_4 , CaTiO_3 and Al_2O_3 , it was found that radiation with heavy ions caused amorphization on ceramic materials. Literally, amorphization is a phase transformation and the phase transfers from a crystalline solid to a solid that lacks any long-range order, but still maintains a certain degree of short-range order.

The primary radiation damage is displacement of one or more atom species and the Frenkel (vacancy-interstitial) pairs are formed consequently. In other words, each atomic displacement event produces a pair of defects known as a Frenkel pair during irradiation and a Frenkel pair is constituted of an interstitial and a vacancy. Under both ballistic and electronic damage conditions at low temperature, amorphization can occur within a single primary knock-on or proceed through the accumulation of primary displacements defects. When ceramics undergo ion irradiation and transfer from crystalline structure to amorphous, there will be the loss of the identity of individual defects which is due to a uniformly defective state of the entire solid, and the loss of long-range order can be observed from the material's structure [37] [9].

With several years' study on the amorphization induced by radiation, it is obvious that low temperature is much easier for most solids to become amorphous. The

amorphization of ceramic materials usually includes substantial dimensional changes (both swelling and compaction are observed) [37]. In ceramic materials, amorphization seems to be detrimental to materials that have been irradiated, as the crystal-to-amorphous transformation is always accompanied by volume swelling, softening and micro cracking [9, 38].

Aside from amorphization on ceramic materials that can be induced by irradiation, ceramics can undergo mechanical and thermal properties changes, and there are considerable studies that have been done on ceramics materials. The early work reviewed by Wilks [39] showed that Young's modulus of polycrystalline alumina was reduced after irradiation, and the similar example was found in MgO. Besides that, it was found by Picot et al. [40] that the monizate material underwent material softening with a hardness reduction of around 60% compared with the pristine monizate material. The reduction in hardness in this material is due to irradiation induced amorphization that results in a lower density structure and eventually the material becomes softened. These degradation phenomena in mechanical properties indicate that the mechanical properties can undergo alterations after irradiation. As for reduction in thermal conductivity in ceramics, because of the phonon scattering by point defects and defect clusters that cause displacement damage, the thermal conductivity therefore decreases.

To sum up, ceramics are inorganic, nonmetallic materials, a class that includes solids with both crystalline and glassy atomic structures. When the ceramic materials follow irradiation with energetic particles, even at low doses of energetic radiation, defects may be generated and can provide the possibility to induce changes in physical properties. These changes include transformation from crystalline to amorphization, changes in strength, toughness, electrical and thermal conductivities. However, ceramics include a

large class of solids with various structures ranging from simple to complex, and the atomic defects after irradiation damage are different in their size, chemistry and mobility. Therefore, the understanding of such phenomena is more difficult than the simple responses of metals and it is difficult to predict the evolution of the microstructure of a ceramic after irradiation.

2.4.4 Radiation damage using ion beam

In order to know the effects of ion irradiation on reactor components, a variety of energetic particles are required to conduct the effects. These energetic particles include helium ions and heavy ions. The ion irradiation could produce the damage state and microstructure change. Therefore, the degree to ion irradiation depends on the particle type and the damage rate.

- **Motivation for using ion beams**

In recent years, ion irradiation has become a significant application to support the reactor development programs and to simulate radiation damage. The reason why there is much more interest in ion beam irradiation is due to three aspects: technique, economic and safety. In terms of the technique part, ion beam could be conducted at a well-defined energy, dose rate and temperature. Using ion beam to simulate radiation damage could generate very well-controlled experiment that is difficult to match in reactors as well [41]. From the economic aspect, ion beam has the potential to save time and money and the irradiation parameters (dose, dose rate and temperatures) used in ion beam simulation can be easily adjusted over a wide range of values. The last part and the most important part is that the ion irradiation has rapid accumulation of end of life

doses in a short time. Ion beam irradiation does not need to spend considerable time to reach damage levels in the 1-100 dpa range and generates little or no residual radioactivity. This means the sample could be handled without special precautions. Because of these features, it is much easier to reduce the cycle length and cost [9]. Therefore, using ion beam irradiation is an effective method to simulate radiation damage and this is the reason for its popularity.

- **Advantages and disadvantages of irradiations using various particle types**

Each type of particle has its strength and drawbacks when doing ion beam irradiation to simulate irradiation damage. The general advantages of these particles are well controlled, verification and time and money saving. However, the disadvantages are that charged particle beams are short of transmutation reactions and it is necessary to use raster-scanned beam in some cases. These particles include heavy ions and light ions.

In terms of the heavy ions, they are good at high dose rates as it could accumulate high doses in short times. In addition, the heavy ions could produce a little energy; therefore, it is efficient for the heavy ions to produce dense cascades. However, it still has some drawbacks. The first one is that large temperature shifts are required for the high dose rates. Another disadvantage is that the penetration depth is short and dose rate over the penetration depth vary continuously [9].

As for light ions, He ions is one of the light ions and it overcomes the drawback of other types of irradiation. The penetration depth of He ions can exceed several micron meters at a few MeV, which is much deeper than heavy ions and the damage layer is even. As such, the dose rate varies much less than that of heavy ions. In addition, at this penetration depth, it is easier to assess the mechanical properties such as irradiation hardening that irradiation induces. However, as the recoil energy is related to the size of

ions, the smaller size of He ion causes the smaller recoil energy, which can induce the damage morphology characterized by smaller, more widely spaced cascades than with other ions [9].

- **Practical considerations for radiation damage using ion beams**

In order to set up ion irradiation experiments, a variety of parameters such as energy, current/dose and beam target interaction should be taken into account. Among these parameters, the depth of penetration is the most important one for consideration. According to Ziegler, Biersack and Littmark [42], they did SRIM calculation on stainless steel using protons, helium ions and nickel ions, it is found that this parameter is different between the light and heavy ions over an order of magnitude in this energy range.

2.5 Perovskite structure

A Perovskite type material is a material that has the same type of crystal structure as calcium titanium oxide (CaTiO_3). It was discovered by Gustav Rose and is named after L.A.Perovski, a Russian mineralogist [43]. Many transition metal oxides also exhibit perovskite structure and receive increasing attraction due to some physical properties like high-temperature superconductivity and colossal magnetoresistance observed in these compounds.

The perovskite type material can be expressed as the general chemical formula ABX_3 . In this formula, A and B stand for two cations with very different sizes, and X is an anion that is bond to both. The A cation has larger radius than the B cation, but has similar radius as that on the anion X. Usually, A cation can be rare earth, alkaline earth

and plenty of other large ions, and the smaller B cation is usually a 3d, 4d and 5d transition metal ion such as titanium and manganese. X is the oxygen or a halide ion. In an ideal perovskite structure, A cation is coordinated with 12 oxygen ions to form the cubic structure while B cation bonds with six oxygen forming an octahedral.

Aside from the ideal perovskite structure, the orthorhombic and tetragonal phases are two common structures distorted from the ideal perovskite structure. In general, for the stoichiometric oxide perovskites, the sum of the oxidation states of A and B cations should be equal to six. The “A” and “B” cations can have various charges such as $A^{+1}B^{+5}O_3$, $A^{+2}B^{+4}O_3$ and $A^{+3}B^{+3}O_3$, and **Figure 2** is the example of A and B cations with different charges [44, 45].

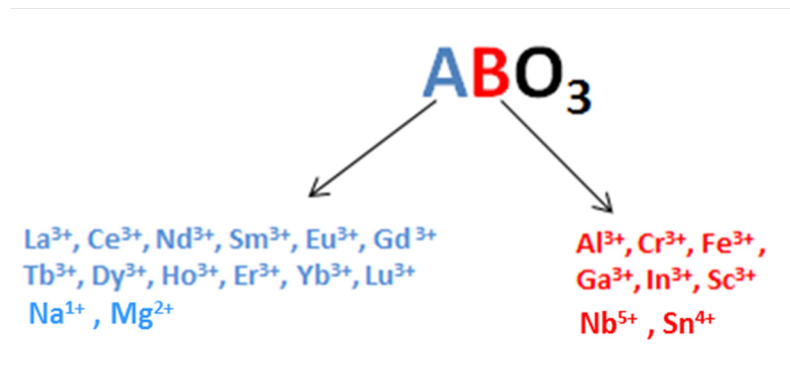


Figure 2. Schematic of compositions of example perovskite structures.

The structure of an ideal cubic perovskite is shown in **Figure 3**. In this figure, the cations that are at the corners of the cube (blue spheres) represent A cations, and the cation in the centre coordinated with oxygen ions (red spheres) is B cation. The space group for cubic perovskites is Pm3m.

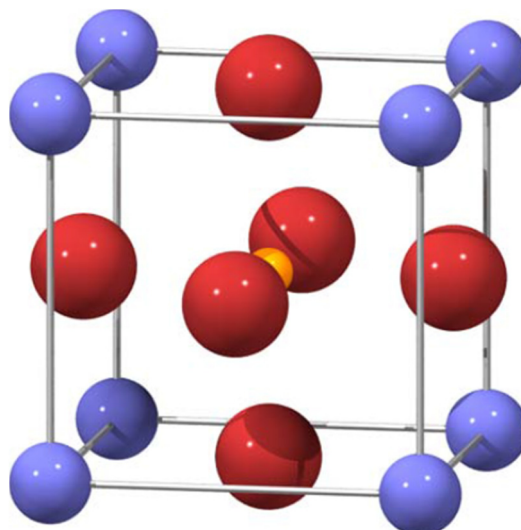


Figure 3. Cubic perovskite unit cell. Blue spheres represent the A cations, yellow spheres represent the B cations, and red spheres represent oxygen anions forming an octahedral [45].

2.5.1 Structure of NdCrO_3 & NdAlO_3

During years of studies, it has been found that the perovskites not only show cubic structure, but also exhibit the Orthorhombic Pnma (Pbnm) structure at room temperature. The distortion from cubic to orthorhombic could be explained as when a cubic lattice is stretched along two of its orthogonal pairs, a rectangular prism will be created and thus with different lattice parameter a , b , and c . Through previous work on examining the XRD pattern of NdCrO_3 [7], it could be found that NdCrO_3 shows the orthorhombic Pnma structure as shown in **Figure 4**.

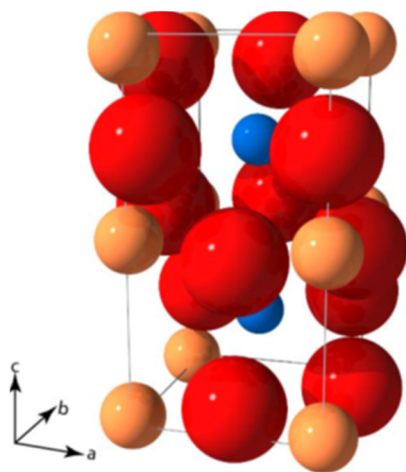


Figure 4. Pnma, orthorhombic perovskite cell. Blue spheres represent the A cations, yellow spheres represent the B cations, and red spheres represent oxygen anions forming an octahedral [45].

Rhombohedral structure with the space group R-3c is another type of structure that can be found in perovskite type materials; and previous work shows that NdAlO_3 exhibits rhombohedral R-3c structure [46]. This distortion from cubic to rhombohedral structure involves a rotation of the AlO_6 octahedra with regard to the cubic structure and the schematic of rhombohedral structure is shown in **Figure 5**.

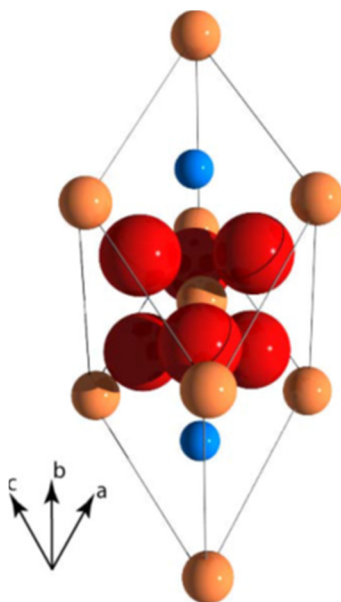


Figure 5. R-3c rhombohedral perovskite unit cell. Blue spheres represent the A cations, yellow spheres represent B cations, and red spheres represent oxygen [45]

2.6 Previous work on PuAlO_3 & PuCrO_3

There is only limited work on the radiation tolerance and thermophysical properties of Pu-doped materials such as PuAlO_3 and PuCrO_3 that can be formed from nuclear fuel and only some theoretical methods have been used for research.

According to Fullarton et al. [6], In order to improve the in-reactor behaviour of fuels, it is possible to add various dopants. Additives like Cr_2O_3 and Al_2O_3 may react with Pu in UO_2 and due to this reaction; precipitates like PuCrO_3 and PuAlO_3 would be formed. Therefore, according to previous work that done by Fullarton et al. [6], a variety of computational methods were used to investigate the behaviour of Pu and also try to understand the formation, structure and thermal properties of PuAlO_3 and PuCrO_3 .

2.6.1 Structure of PuAlO_3 & PuCrO_3

Fullarton et al. [6] did a lot of work to verify the structures of PuAlO_3 and PuCrO_3 and six possible $\text{A}^{3+}\text{B}^{3+}\text{O}_3^{2-}$ analogues were chosen to simulate them. These six phases are LiNbO_3 (R3c)-type structure, GdFeO_3 (Pnma)-type structure, SrTiO_3 ($\text{Pm } \overline{3} \text{ m}$) structure, NdAlO_3 (R-3C)-type structure, LaAlO_3 ($\text{R } \overline{3} \text{ m}$)-type structure and the BiMnO_3 (C2/c)-type structure. These selected structures are all related to the SrTiO_3 perovskite structure and either show distortions or displacements over the anion or cation sublattices. The reason to choose these structures is that these structures are the possible perovskite-related structures with the various families of structures, which allow the lowest energy structure to be identified.

Through computational method, for PuCrO_3 , the most stable structure that was predicted was the orthorhombic GdFeO_3 -type phase shown in **Figure 6**. As of the six

structure analogues that are mentioned above, both methods lead to negative reaction enthalpies for LiNbO_3 -type, BiMnO_3 -type, GdFeO_3 -type structures, indicating they are stable. Among these structures, it was found that the GdFeO_3 -type structure had the lowest formation enthalpy via both empirical and DFT methods. As for PuAlO_3 , the similar method was investigated to predict its structure and the predicted most stable structure could be both orthorhombic and the rhombohedral structure of PuAlO_3 .

As mentioned before, it is found from literatures [46, 47] that the structures of NdCrO_3 and NdAlO_3 are orthorhombic and rhombohedral. The predicted structures of PuCrO_3 and PuAlO_3 are orthorhombic and rhombohedral as well. Therefore, the structures are in agreement with each other suggests Nd can be used as for Pu.

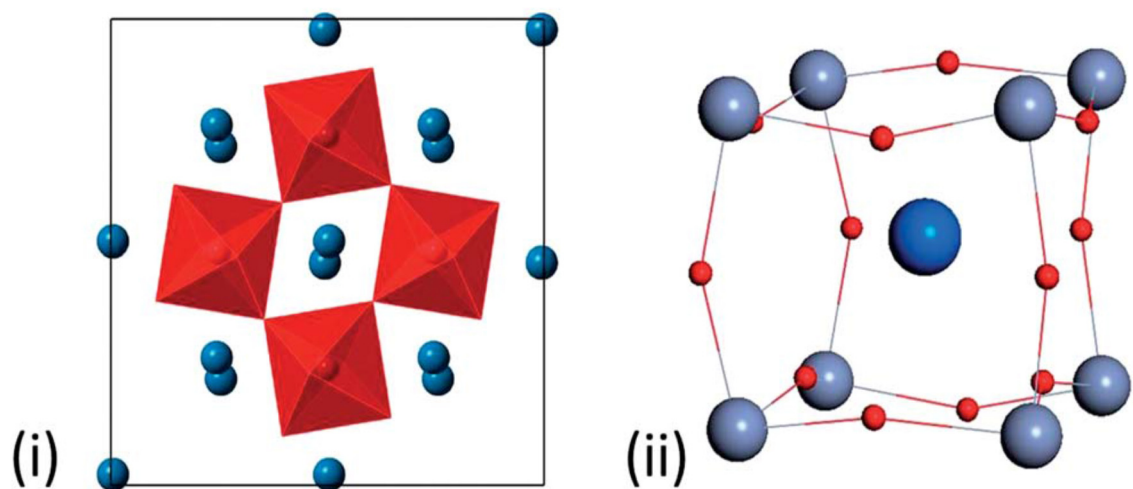


Figure 6. The predicted lowest energy structure of PuCrO_3 – the Pnma orthorhombic structure (i) illustrates the structure viewed down the z -axis, highlighting the Cr–O octahedral distortions (red polyhedra) around the Pu ions (blue).

(ii) Illustrates the perovskite single unit cell with oxygen distortion around the Cr ions (grey) [6].

2.6.2 Thermal stability of PuCrO₃ and PuAlO₃

Thermal stability is the stability of a material at high temperatures. In most cases, if a material with more stability, it has more resistance to decomposition at high temperatures.

According to previous work [6], the predicted structure of PuCrO₃ and PuAlO₃ are orthorhombic and rhombohedral, which are perovskite-type materials. As for the thermal stability of perovskite-type materials, it is found that the nature of position of A and B cation are responsible for the thermal stability of perovskite oxides (ABO₃). The thermal stability of perovskite oxides is also related to the type of cation at the B position [48]. For example, when studied the thermal stability of a series of LaBO₃ (B=V, Cr, Mn, Fe, Co, Ni), it can be established as LaNiO₃ < LaCoO₃ < LaFeO₃ < LaMnO₃ < LaCrO₃ ~ LaVO₃ [49].

However, in terms of the thermal stability of PuCrO₃ and PuAlO₃, limited research can be found and therefore further investigation is required to study this property.

2.6.3 Thermal conductivity of PuCrO₃ and PuAlO₃

The prediction of thermal conductivities through computational methods was also done by Fullarton et al. [6] on the stoichiometric UO₂, PuCrO₃ and PuAlO₃. The temperature range investigated was from 300 to 1600 K and **Figure 7** [6] describes the variation of thermal conductivity of the three phases.

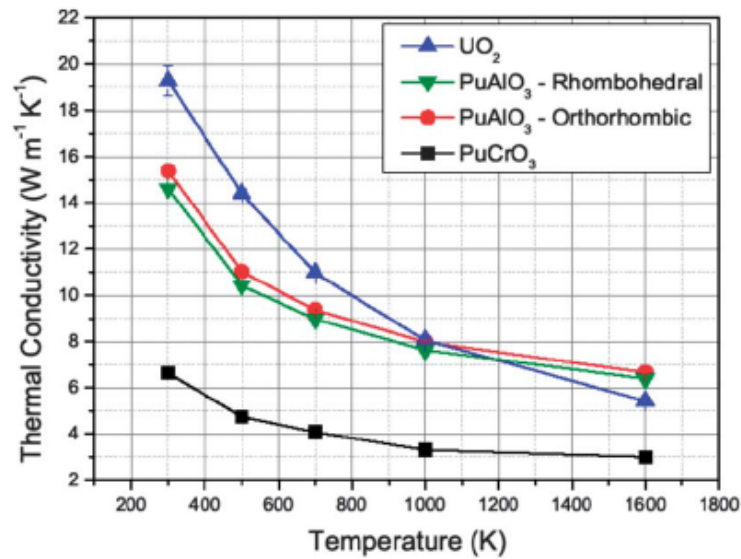


Figure 7. variation of thermal conductivity with temperature of stoichiometric UO₂, PuCrO₃ and PuAlO₃ (both rhombohedral and orthorhombic lattices) [6].

From **Figure 7**, it could be found that the thermal conductivity of PuCrO₃ had a notably lower thermal conductivity than that of UO₂ from 300 to 1600K, which is similar to LaCrO₃ [50]. The lower thermal conductivity of PuCrO₃ may have a distinct knock-on effect upon its supposed formation in the rim region of a standard doped fuel, or dispersed through a MOX fuel pellet. The thermal conductivity of both structures of PuAlO₃ was predicted to have a lower thermal conductivity than UO₂ at low temperature but a higher thermal conductivity at elevated temperature.

Therefore, it was concluded by Fullarton [6] that the presence of PuCrO₃ could decrease the thermal conductivity of UO₂ fuel, and this will have implications for the thermal behaviour of Cr-doped fuels and will therefore have knock-on effects on the gas release properties, structure and fission product accommodation. It is described in literature [6] that decreases in thermal conductivity of a pellet will lead to a greater centre line pellet temperature with equivalent rim/clad temperatures. The enhanced fuel temperatures may further increase fission gas release and this may increase the rod internal pressure.

This can lead to microstructural evolution and/or a change in fracture behaviour. Regarding to the safety, the release of radioactive gases from UO_2 to the free volume of fuel rod would decrease the safety margin of a nuclear plant. In addition, PuAlO_3 only has the higher thermal conductivity than that of UO_2 when the temperature is $> 1000^\circ\text{C}$. Hence, understanding the thermal conductivity of PuAlO_3 and PuCrO_3 is vital and may lead to significant impact on fuel pellets design and subsequent waste form production.

2.7 Summary

The additives in nuclear fuel allow higher burn up and in turn can improve the economic efficiency. However, the formation of new phases because of interaction of fuel dopants (such as Cr_2O_3 and Al_2O_3) and Plutonium will have some impacts on nuclear fuels and the resulting waste form. In this project, in order to understand the thermophysical properties and radiation tolerance of PuCrO_3 and PuAlO_3 and understand what impact these phases will have on UO_2 fuel; NdCrO_3 and NdAlO_3 were selected as surrogates to simulate the Pu-doping phases. These two perovskite-type materials were investigated individually, and a comparison on the properties of NdCrO_3 and NdAlO_3 with Pu-doping phases were made through characterizations on irradiated NdCrO_3 and NdAlO_3 to predict the radiation tolerance of PuCrO_3 and PuAlO_3 as well as thermophysical properties of these species.

Chapter 3 Experimental

3.1 Introduction

As mentioned in previous chapter, due to the formation of PuCrO_3 and PuAlO_3 in UO_2 fuel. It is important to understand the thermophysical properties and radiation tolerance of these two phases. To understand these properties, the measurement of thermal conductivity, ion beam irradiation and characterizations on irradiated samples are needed.

Before some measurements and characterizations can be done on neodymium chromate and neodymium aluminate, it is necessary to synthesise these ceramic powders and have them pressed and sintered.

In this chapter, sample preparation of neodymium chromate and neodymium aluminate is described, followed by the experimental principle and procedure of thermal conductivity, ion beam irradiation and characterizations such as x-ray diffraction, grazing incidence x-ray diffraction, scanning electron microscope, Raman spectroscopy, Nano-indentation and thermal annealing.

3.2 Sample preparation

To prepare samples for thermophysical properties and ion beam irradiation, samples should go through two steps: powder synthesis and ceramic preparation. Each step is introduced in detail below.

- **Powder Synthesis**

First, neodymium chromate (NdCrO_3) and neodymium aluminate (NdAlO_3) powders need to be synthesised. Generally, there are two methods to synthesise ceramic powders, and these two approaches are top down synthesis and the bottom-up synthesis.

Table 1 Ceramic Powder Synthesis approaches [51].

Top-down approach	Bottom-up approach
Solid state reaction	Co-precipitation
Thermal decompositions of solid	Hydrothermal synthesis
Redox reaction of a solid	Sol-gel synthesis

In this experiment, neodymium chromate and neodymium aluminate powders were prepared using the Co-precipitation method. Through Co-precipitation synthesis, chemicals were weighed, mixed, dried and calcined to produce the crystalline powders. Before making ceramic, ball milling was utilized on these powders to reduce the particle size and produce the fine powder.

- **Ceramic Preparation**

In order to make a ceramic, the fine powder from powder synthesis underwent the conventional sintering process. Specifically, sintering is known as a heat treatment process to consolidate powders into a dense compact [52]. The individual powder particle grains grow and compact with each other forming a dense pellet. The procedure of this sintering method follows three steps. First, the surface of the mold is applied with lubricant to reduce the friction between the powder and surface of the mold. Therefore, it is much easier to remove the pellet and protect the edge of the pellet from cracking when ejecting from the mold. Next, the powder is uniaxially pressed in a rigid die under pressure at 5MPa. The as-prepared pellet should be sufficiently compacted to withstand ejection from the die. Eventually, the pellet will be sintered at high

temperature (e.g., $\sim 1600^{\circ}\text{C}$) in furnace for a certain period of time. The ceramic should have a high density after final sintering step.

Sometimes the sintered sample is not sufficiently dense to do the ion beam irradiation after the conventional sintering process. Therefore, it is necessary to apply cold isostatic press (CIP) on the porous sample after uniaxial press before sintering. Specifically, cold isostatic pressing is a material processing method. The pellet is sealed in a forming mold with low deformation resistance such as a rubber bag to apply liquid pressure. With this method to apply the pressure, the pressure can be distributed uniformly over the compaction material contained in a rubber bag. The benefit of isostatic pressing is that the pellet is compacted with the same pressure in all directions, and since no lubricant is needed, high and uniform density can be achieved [53]. Then, the CIPed sample can be sintered at the target temperature and the final ceramic will be dense.

Specifically, in this experiment, in order to synthesise neodymium chromate (NdCrO_3) and neodymium aluminate (NdAlO_3) powders, neodymium nitrate hexahydrate ($\text{Nd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$), chromium nitrate nonahydrate ($\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) and aluminium nitrate nonahydrate ($\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) are required. Weighing stoichiometric amounts of both of the chemicals and adding the amount of water to mix them together in a plastic beaker. Thereafter, heating and stirring the mixed chemicals to dryness on a hot plate at $\sim 120^{\circ}\text{C}$. After addition of 25% ammonia solution to adjust the pH to ~ 9.5 , the dried powder was then calcined in air for 5 hours at 750°C . The calcined powder was then milled using yttria-stabilized zirconia balls in cyclohexane overnight and dried at $\sim 120^{\circ}\text{C}$. The powder was uniaxially pressed at 5MPa and NdCrO_3 was sintered to 1600°C directly for 26 hours to provide $\sim 1\text{g}$ pellets ($\sim 10\text{ mm}$ diameter). NdAlO_3 was

cold isostatic pressed (CIPed) first and sintered at 1600°C for 26 hours. Sample density was measured in distilled water using Archimedes' method (Chapter 4, Table 4).

Various sintering temperatures following cold isostatic pressing were trialled on these samples in order to find the best condition for preparing dense pellets. As shown in **Table 2**, NdCrO₃ and NdAlO₃ have been sintered at four different temperatures (1400, 1500, 1600, 1700°C) with CIP and without CIP.

SEM images of the samples prepared at different temperatures reveal that 1600° produces the densest pellets for both NdCrO₃ and NdAlO₃ materials. Sintering is known as a heat treatment process to consolidate powders into a dense compact. Sometimes the sintered sample is not sufficiently dense to do the ion beam irradiation after the conventional sintering process and density is extremely important when it comes to analysis of the post irradiated pellet. e.g., cross-sectional SEM requires a high density in order to see the very thin damaged layer. Therefore, it is necessary to apply cold isostatic pressing (CIP) after uniaxial pressing and before sintering. Various sintering temperatures (1400, 1500, 1600 and 1700) following cold isostatic pressing were investigated in order to find the best condition for preparing dense pellets. SEM images of the samples prepared at different temperatures reveal that 1600 °C produces the most dense pellets for both NdCrO₃ and NdAlO₃ materials. Cold isostatic pressing was found to have an effect on the resulting crystal structure for NdCrO₃ and was therefore not utilized (**Figure 8 and 9**). Thus, NdAlO₃ was CIPed first then was sintered, while NdCrO₃ was sintered directly. With the CIP, it seemed produced a change (an extra peak on the XRD trace) in the resulting NdCrO₃ pellet. It was not possible to index the extra peak at 2θ which appeared in the CIPed sample. SEM also confirmed a single phase material via a backscatter detector which showed no contrast and thus no

compositional variation. XPS was used to assess the chromium oxidation state which appeared to be only Cr^{3+} in both CIPed and unCIPed samples. We therefore cannot currently assign this extra peak without further work.

Table 2. The list of different sintering temperature for CIPed and no CIPed NdCrO_3 and NdAlO_3 .

	CIP				NO CIP			
	1400	1500	1600	1700	1400	1500	1600	1700
NdCrO_3	✓	✓	✓	✓	✓	✓	✓	✓
NdAlO_3	✓	✓	✓	✓	✓	✓	✓	✓

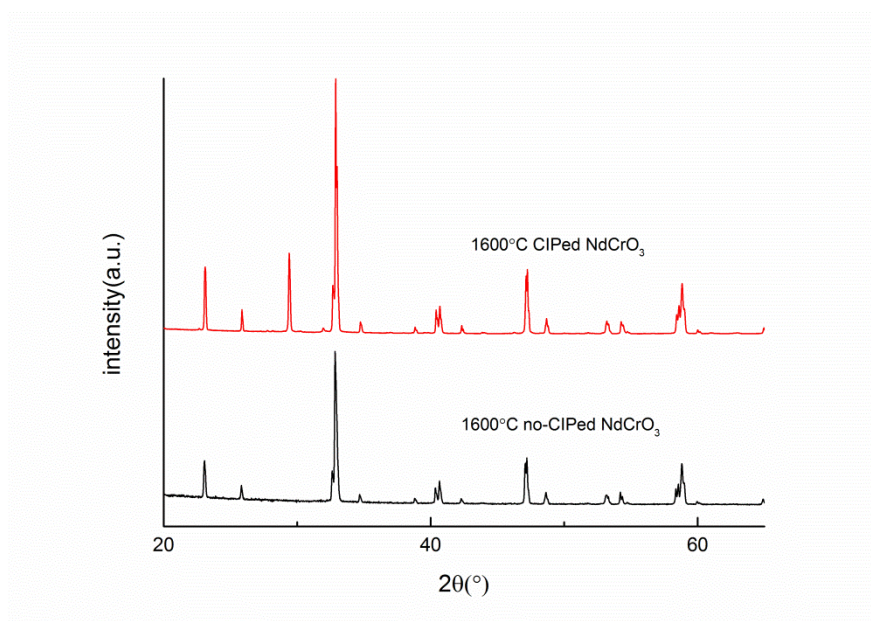


Figure 8. XRD pattern of CIPed NdCrO_3 and no- CIPed NdCrO_3 that sintered to 1600°C .

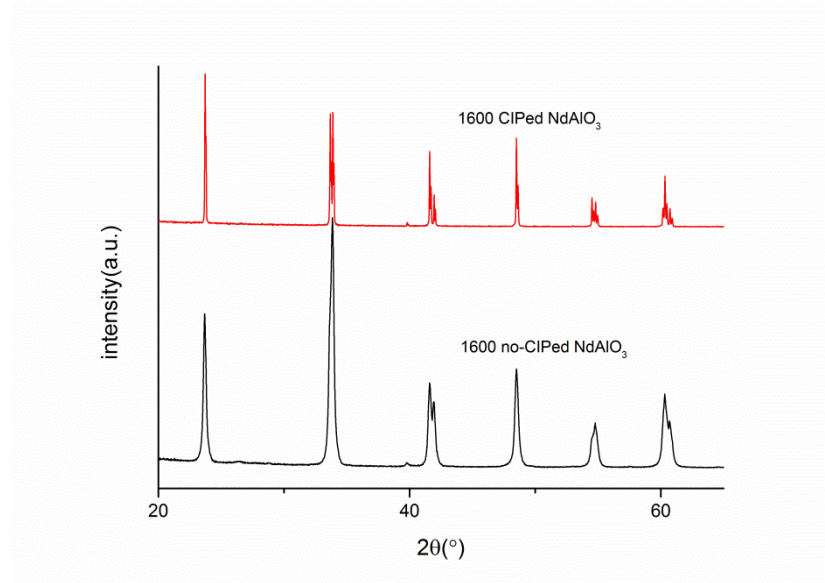


Figure 9. XRD patterns of CIPed NdAlO₃ and no- CIPed NdAlO₃ that sintered to 1600°C.

3.3 Thermo-physical analysis

Thermal conductivity can be determined according to the equation [54]:

$$k = \alpha \cdot \rho \cdot Cp$$

k - Thermal conductivity (W/m*K)

α - Thermal diffusivity (mm²/s)

P - Thermal expansion (kg/m³)

Cp - Specific heat capacity (J/ (kg*K))

Therefore, in order to understand the thermal physical properties of NdCrO₃ and NdAlO₃, thermal diffusivity, thermal expansion and specific heat capacity of these two materials were measured by laser flash system (NETZSCH LFA-467), Dilatometry (NETZSCH DIL 402C) and simultaneous thermal analysis (NETZSCH STA 449 F1 Jupiter).

3.3.1 Specific heat capacity

Specific heat capacity of NdCrO_3 and NdAlO_3 were measured directly through simultaneous thermal analyser (NETZSCH STA 449 F1 Jupiter). The program was running from room temperature to 1200°C . The heating rate was constant at 20K/min with high purity argon was used with a continuous flow rate of 20 ml/min . A sample carrier, which is placed in a furnace of cylindric geometry, holds reference and sample crucibles (shown in **Figure 10**); thermocouples are utilized to detect temperatures between each crucible. Three measurements (baseline, reference test and experimental sample test) are necessary for calculating the specific heat capacity. The baseline is used to remove system bias from the data, and the reference test allows the comparison to an experimental sample. Overall, three tests must be performed for each test sample. By analysing the baseline, sapphire calibration and sample curve, the specific heat capacity of the sample can be determined at different temperature points. For the as-prepared samples, the weight should be similar as the reference sample

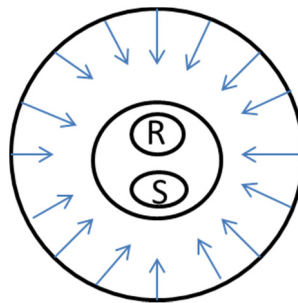


Figure 10. Diagram of heating pattern and system geometry (R=reference S=sample)

3.3.2 Thermal expansion

The linear thermal expansion coefficient ($\Delta L/L_0$) of NdCrO_3 and NdAlO_3 were measured using Dilatometry (DIL 402C). Dilatometry can measure linear thermal

expansion, coefficient of thermal expansion, and volumetric expansion, etc. The DIL 402C (Netzsch, Germany) that was used in this experiment was a pushrod dilatometry (**Figure 11**). It consists of furnace, measurement system, oxygen trap system and sample holders. To perform thermal expansion analysis, NdCrO_3 or NdAlO_3 was inserted into a sample holder within a movable furnace, a pushrod was positioned directly against the sample, the sample was directly heated to 1200°C and the heating rate was 10K/min . There were two procedures included in this measurement, first was measuring the thermal expansion of the standard sample (Alumina). Then, the sample was inserted into the sample holder to do the measurement. All linear thermal expansion data were based on this standard. In order to meet the requirement of dilatometry measurement, samples were cut to about 15 mm length bars which is similar as the standard reference.

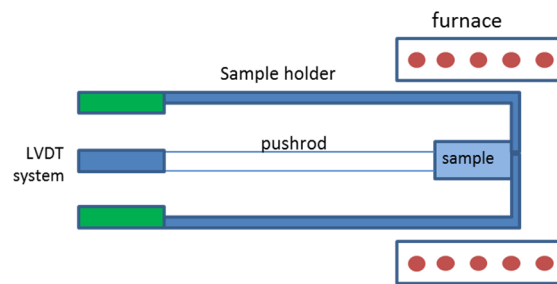


Figure 11. Schematic illustration of the pushrod dilatometer.

3.3.3 Thermal diffusivity

Thermal diffusivity of NdCrO_3 and NdAlO_3 were measured using NETZSCH LFA-467 HT (Netzsch, Germany) for a pellet of about 10 mm diameter with a thickness of around 2 mm. The measurement was conducted in a temperature range from room temperature

to 1100°C and the measurements were carried out in a standard sample holder (Ø 10 mm). The sample was measured five times at each temperature step and the sample was coated with graphite to obtain optimal absorption and emissivity of sample surfaces. The schematic illustration of the sample chamber is shown in **Figure 12**. The sample with sample holder is placed vertically to the pulse and the detector, and during the measurement, a short energy will be provided to heat the front surface of a plane-parallel and the infrared (IR) detector on top measured out the temperature rate on the backside of the sample. When an infrared (IR) detector measures the resulting temperature excursion of the rear face, the thermal conductivity is calculated. There are different types of sample holders to fit with the sample, and the sample can be round or square. The higher the thermal diffusivity, the faster the temperature-increasing rate is on the backside of the sample. Before the measurement, the thickness and the density of the test sample are required.

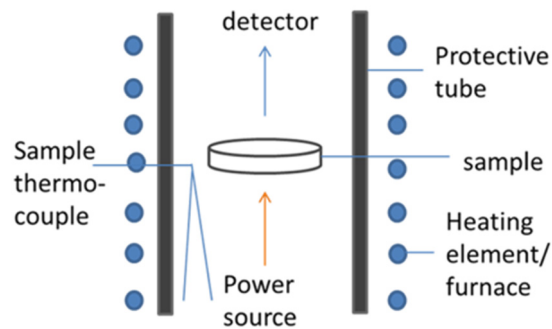


Figure 12. Schematic illustration of the sample chamber in LFA 467.

3.4 Characterization

Characterization was undertaken to determine crystal structure, phase purity, phase composition and mechanical properties of pristine materials as well as investigate the

changes between pristine materials and irradiated materials. Therefore, a series of characterization techniques were utilized to study on the microstructural properties of NdCrO₃ and NdAlO₃ and each of them is introduced separately below.

3.4.1 X-ray diffraction

X-ray diffraction (XRD) was used to identify the crystal structures, phases, lattice parameters and crystallinity. A crystal consists of a periodic arrangement of the unit cell into a lattice, and a set of parallel layers with a constant distance in a lattice. The peak intensity and position are determined by the crystal structure of materials. X-ray diffraction is used to measure the spacing between different layers of crystals using the X-ray radiation. According to the Bragg's law [55]:

$$n\lambda = 2d\sin\theta$$

Where n is a positive integer, λ is the wavelength of incident wave, d is the interplanar distance and θ is the scattering angle.

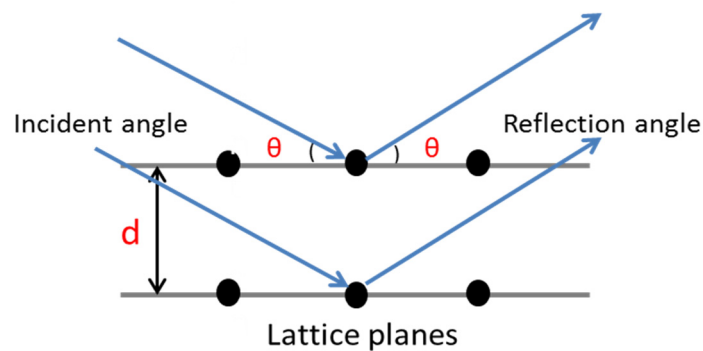


Figure 13. Schematic illustration of the Bragg's law.

By using the XRD technique, XRD patterns of NdCrO₃ and NdAlO₃ were measured using a BRUKER D8 Advance diffractometer, utilizing Cu K $\alpha_{1,2}$ radiation and a SOL-

XE energy dispersive detector over an angular range $10\text{-}65^\circ$ 2θ with a step size of 0.02° and accounting time of 5s per step.

3.4.2 Grazing Incidence X-ray Diffraction

Grazing incidence X-ray diffraction (GI-XRD) is a technique that can analyse the surface, interface and thin-film. Traditionally, X-ray diffraction uses large incident angle, which causes an incident X-ray beam to penetrate deep into a material. However, when using grazing incidence X-rays, the incident X-ray beam could be limited to the surface [56]. As for materials irradiated with Au-ions, the damaged layer is at the top layer of the pellet that is near the surface; therefore, grazing incidence X-ray diffraction (GI-XRD) is required for these irradiated materials for characterization. The schematic of the symmetric GI-XRD geometry is shown in **Figure 14** and shows the incident and diffracted beams.

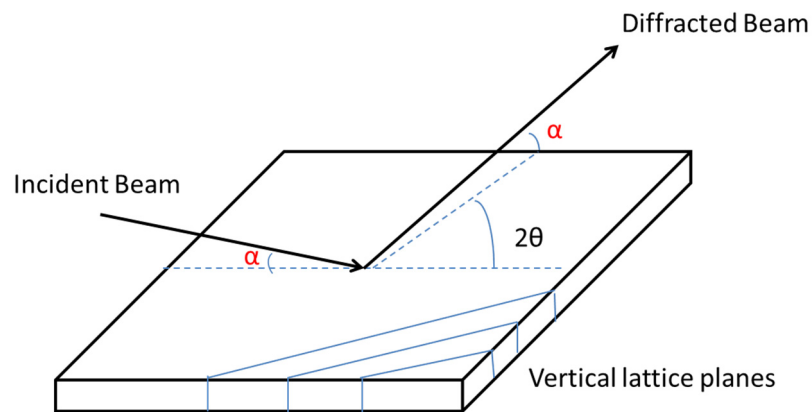


Figure 14. Schematic illustration of the symmetric GI-XRD geometry.

By using GI-XRD techniques, XRD patterns of irradiated NdCrO_3 and NdAlO_3 , which were irradiated with Au-ions at different fluences, were measured using a BRUKER D8 Advance diffractometer, utilizing $\text{Cu K}\alpha_{1,2}$ radiation and a SOL-XE energy dispersive

detector over an angular range $10\text{--}65^\circ$ 2θ with a step size of 0.02° , and accounting time of 5s per step. Only sample surface, the damaged layer, can be characterized by the Grazing incidence X-ray diffraction. The incident angles were chosen as 0.5° , 1° , 2° , 5° to achieve the extinction of X-rays approximately $1\text{--}3\ \mu\text{m}$ below the surface, the Au-ions irradiation-damaged thickness.

3.4.3 Scanning Electron Microscopy (SEM)

In order to identify the microstructural, phase purity, phase compositions, porosity of the pristine material and analyse the damaged layer of cross-sectioned NdCrO_3 and NdAlO_3 following Au- and He-ion irradiation at various fluences, scanning electron microscope (SEM) was used (**Figure 15**). A scanning electron microscope (SEM) is a kind of electron microscope. Specifically, it generates a focused beam of electrons (back-scattered electrons, secondary electrons and transmitted electrons) to interact with a specimen and scan the surface of the sample; as such, a variety of signals can be detected and can create an enlarged image which contains the surface topography of the sample. In a typical SEM, an electron beam is emitted from an electron gun. Among these kinds of electrons that produced by SEM, the SEM with secondary electron, due to the narrow electron beam, can produce high-resolution images and it is useful to understand the surface structure of a sample. With back scattered electrons (BSE), it is readily to distinguish different chemical compositions by observing high-resolution contrast. Besides this, in order to decide the crystallographic structure of the sample, electron backscatter diffraction (EBSD) image is required [57].

In this experiment, pristine and irradiated samples were examined by A Zeiss Ultra Plus scanning electron microscope operating at 15kV and equipped with an oxford

instruments X-Max 80 mm² SDD X-ray microanalysis system. The pristine materials and cross-sectioned irradiated samples were mounted in an epoxy resin and polished to 1 µm ceramic finish followed by EBSD polish (An EBSD polish is the preparation of samples for electron backscatter diffraction (EBSD). It is similar to routine preparations; however, to meet the requirements of EBSD analysis, all surface defects on the sample should be removed and it is necessary to have superior surface flatness. An EBSD polish is achieved by use of an appropriate polishing cloth for samples to minimize sample deformation and maximize sample flatness). A carbon film (~ 3 nm) was deposited onto the polished surface. Variations in crystallography contrast at high resolution were observed in the SEM using backscattered electron channelling contrast imaging with an ASB (angular selective backscatter) detector [58].

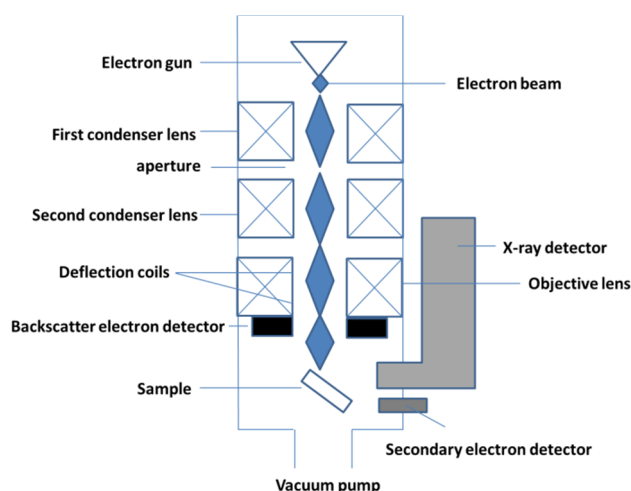


Figure 15. Schematic diagram of the principle of SEM.

3.4.4 Raman Spectroscopy

Raman spectroscopy is a form of vibrational spectroscopy. It can provide the chemical and structural information of samples through the shift in wavelength of the inelastic scattering of photons. Generally, Raman scattering is the inelastic scattering of photons, and there always has frequency changes for the scattered photons. When photons are

scattered from an atom or molecule, most of these photons experience elastically scattering, called Rayleigh scattering. The scattered photons, under the Rayleigh scattering, have the same energy, frequency and wavelength as the incident photons. However, there will be a small portion of photons will undergo frequency change after scattering; some inelastic scattered light photons have higher frequency (Anti-strokes shift) and others have lower (Strokes shift) frequency than that of the incident photons (**Figure 16**). Raman spectroscopy is also an effective technique for studying the effect of ion-beam irradiation to complement the XRD analyses as it has a shorter correlation length scale of about a few unit cells. It was performed on cross-sectioned irradiated pellets at various damage depths to probe the un-irradiated and irradiated material [59]. In this experiment, in order to collect Raman spectra, a Renishaw inVia Raman spectrometer equipped with the Argon ion laser (514 nm) and a Peltier cooled CCD detector was used. Strokes shifted Raman spectra were collected in the range of 150-600 cm^{-1} with a spectral resolution of 1.7 cm^{-1} for the 1800 l/mm grating. The spot size was around 1.5 μm for 50 $\times$ magnification. Samples (pristine materials and Cross-sectioned irradiated materials) for Raman spectroscopy were mounted in an epoxy resin and were polished to $\sim 1 \mu\text{m}$ ceramic finish.

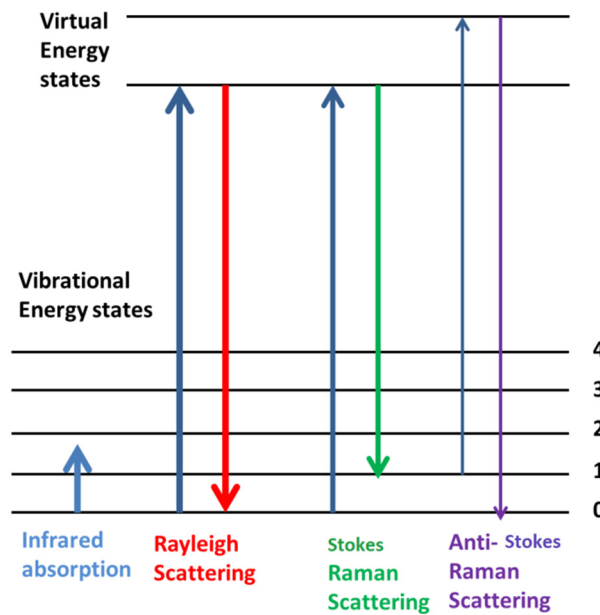


Figure 16. Energy level diagram showing the states involved in Raman level.

3.4.5 Nano-indentation

In order to determine the hardness variation between Au-ion irradiated NdCrO_3 and NdAlO_3 and un-irradiated materials, Nano-indentation was utilized. Nano-indentation is the technique that is widely used for measuring the mechanical properties of a material at limited scales and analysing the hardness variation of materials after ion irradiation [60-62]. A Nano instrument's Nano-indenter examined the change of hardness and elastic modulus after irradiation. A very small tip was brought into the material surface to produce an imprint and this is always with applying an increasing load up to a targeted value (**Figure 17**). Before making indentation acquisition, an optimal area without scratches or impurities should be chosen using an optical microscope. Thereafter, the measurement could then start.

In our experiment, an Aglient Nano Indenter G300 [63] with MTS Test Works 4 software [64] was used to measure the surface hardness of the un-irradiated and irradiated pellets. The Nano-indenter has displacement resolution of < 0.01 nm and a

load resolution of around 50 nN. A minimum of fifteen indentations were made using a Berkovich indenter for both irradiated and un-irradiated samples.

The depth limit, in this experiment, was set to go into both materials is 1 μm and the indenter tip was driven into the sample by applying an increasing load up to a targeted value. Thereafter, the sample shows relaxation with the gradual decrease of the measured load. The reason we choose 1 μm rather than 2 μm as the depth limit is that when the indenter tip is given the load to drive into sample, there will be plastic deformation and the range of plastic deformation is considered to be about 4 times the indent depth [65] and there will be an effect zone. Therefore, choosing 1 μm as the depth considered enough to interrogate the hardness of irradiated zone. Nano-indentation is only used on Au ions irradiated samples as the damage depth for sample irradiated with He ions is very deep around 15 μm and difficult to probe.

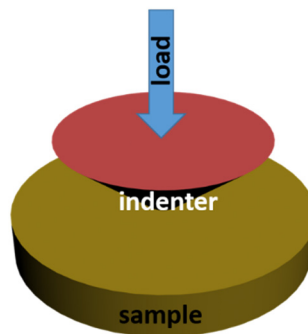


Figure 17. Schematic illustration of Nano-indentation measurement.

3.4.6 Thermal annealing

Thermal annealing is a kind of heat treatment applied on a material to change the microstructural properties of a material and further alter a material's mechanical

properties such as hardness and strength [66]. The process of thermal annealing is heating a material to above its recrystallization temperature, maintaining at a suitable temperature for a period, and then slowly cooling.

There are three stages included in the annealing process: recovery, recrystallization and grain growth. During the recovery stage, there is no change on the grain size and shape and recovery always occurs at the lower temperature stage of annealing process. At the second stage, recrystallization, new strain-free grains starts to form and replace those deformed grains due to the internal stresses [67]. Grain growth is the third step following recrystallization; during this stage, the mechanical properties of a material will undergo some variations.

In this project, thermal annealing was carried out on damaged samples with the highest fluence (10^{15} ions/cm²) of Au ions. These irradiated samples were sequentially re-sintered to various temperatures (600, 800, 1000, 1200 and 1600°C), and then compared with the un-irradiated material using GI-XRD. Specifically, for thermal annealing, each sample was heat treated at 600, 800, 1000, 1200 and 1600°C 2 hours.

3.5 Ion beam irradiation

As alpha decay damage from plutonium in the material, therefore, alpha decay is selected for simulating. In order to simulate effect of alpha decay, two sets of ion irradiation experiments were carried out on the samples. The ions that used for irradiation were 12 MeV Au ions to simulate alpha recoil nucleus that has the energy between 70 and 100 keV; and 5 MeV He ions to simulate alpha particles. The kinetic

energy of these particles is deposited in the host material by Ballistic process (E_{nuc}) and ionization and electronic excitation process (E_{elec}) [34].

Although Au ions have a similar mass with alpha recoils, they can penetrate ~ 40 nm at energy of ~ 70 -100 keV (recoil atom energy) [40], which restricts the characterization techniques that can be utilized for the damaged layer. Therefore, in our experiment, increasing the energy of Au ion to 12 MeV provided a reasonable thickness (~ 3 μm) of damaged material for characterization but it does affect the ratio of f_{elec} and f_{nuc} . Although this may affect the actual damage mechanism, we expect amorphization from Au ions and recoil atoms to occur at similar fluences. The irradiation fluence levels ranged from 10^{13} to 10^{15} ions/ m^2 for Au ions, and 10^{16} to 10^{17} ions/ cm^2 for He ions. According to Picot et al. [40], the selected displacement damage amount was used to simulate a cumulative radiation dose and compared to that produced about several hundreds of years in a waste form matrix containing 10 oxide wt% minor actinides and this corresponds to a nuclear damage on the order of 1 dpa.

Ion irradiation was carried out at ANSTO at room temperature; ANTARES (Australian National Tandem for Applied Research Accelerator) is used for gold irradiation and STAR (Small Tandem for Applied Research) accelerator is selected for helium irradiation. ANTARES accelerator is shown in **Figure 18**. The Energy fraction (f_{elec} and f_{nuc}), depth profile and the main characteristics for irradiated NdCrO_3 and NdAlO_3 based on SRIM 2013 [40, 68] are indicated in **Table 3**.

Displacement per atom (dpa) as a function of irradiation depth was calculated for both Au- and He-ions at a fluence of 10^{15} and 10^{17} ions/ cm^2 and they are plotted in **Figure 19 and 20**.



Figure 18. Australia National Tandem Research (ANTARES) Accelerator [69].

Table 3. Energy fraction (f_{elec} and f_{nucl}), depth profile and the main characteristics for irradiated $NdCrO_3$ and $NdAlO_3$ based on SRIM 2013.

Sample (Au)	Peak damage depth (um)	DPA			f_{elec} (%)	f_{nucl} (%)
		10^{13} ions/cm ²	10^{14} ions/cm ²	10^{15} ions/cm ²		
$NdCrO_3$	1.32	0.0292	0.292	2.92	72.65	27.35
$NdAlO_3$	1.28	0.0245	0.245	2.45	74.82	25.18

Sample (He)	Peak damage depth (um)	DPA		f_{elec} (%)	f_{nucl} (%)
		10^{16} ions/cm ²	10^{17} ions/cm ²		
$NdCrO_3$	15.4	0.122	1.220	98.09	1.91
$NdAlO_3$	12.8	0.133	1.332	98.14	1.86

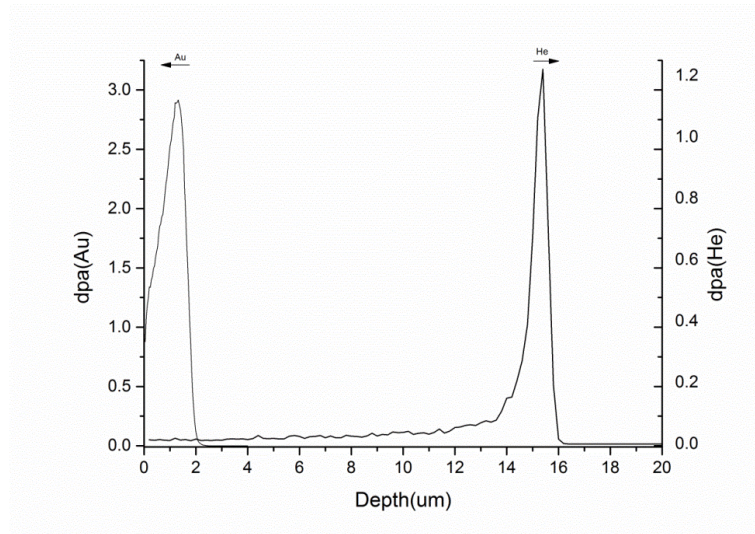


Figure 19. Displacement per atom as a function of irradiation depth of NdCrO₃ for Au or He ions calculated using SRIM 2013.

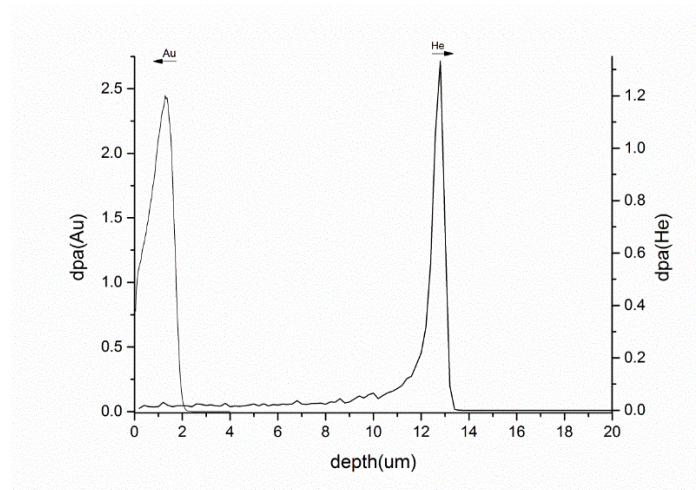


Figure 20. Displacement per atom as a function of irradiation depth of NdAlO₃ for Au or He ions calculated using SRIM 2013.

Chapter 4 Characterization of pristine NdCrO₃ and NdAlO₃

4.1 Introduction

As mentioned in Chapter 1, PuCrO₃ and PuAlO₃ are likely to be formed in UO₂ fuel due to the reaction of additives (Cr₂O₃ and Al₂O₃) with Pu in UO₂ fuel, and the presence of these two Pu-doping phases may have some impacts on the used fuel when stored as waste for a long time. Therefore, it is necessary to investigate the thermophysical properties and radiation tolerance of PuCrO₃ and PuAlO₃. However, PuCrO₃ and PuAlO₃ are radioactive and thus Nd was selected as the surrogate of Pu because of their ionic radii and oxidation state similarity. Thereafter, experiments and characterizations were carried out on NdCrO₃ and NdAlO₃.

In Chapter 3, co-precipitation method was utilized to synthesise the powder of neodymium chromate and neodymium aluminate and conventional sintering process was applied to make ceramic pellet.

Before measuring the thermal conductivity and doing ion beam irradiation on these as-prepared samples, it is necessary to characterise the NdCrO₃ and NdAlO₃ materials by confirming their crystal structure, purity and density in experiment. Characterizations such as X-ray diffraction (XRD), scanning electron microscopy (SEM) and Raman microscopy were applied to make sure the samples were single phase.

4.2 Results and discussion

4.2.1 X-ray diffraction

The X-ray diffraction patterns of neodymium chromate (NdCrO_3) and neodymium aluminate (NdAlO_3) sintered at 1600°C are shown in **Figure 21 and 22**. It is clear from **Figure 21** that NdCrO_3 exhibits orthorhombic structure with Pnma space group which matches the standard pattern of NdCrO_3 and the pattern of PuCrO_3 [7]. **Figure 22** shows the XRD pattern of NdAlO_3 and it indicates that NdAlO_3 exhibits rhombohedral structure which matches the standard pattern of NdAlO_3 and PuAlO_3 [70]. For both XRD patterns, the peaks are sharp and this indicates the materials were well crystallized. For both of these XRD patterns, the baselines are smooth and no impurity peaks are observed, indicating the high purity of the as-prepared samples.

The predicted most stable structure for PuAlO_3 was orthorhombic as predicted by Fullarton [6] and rhombohedral as predicted by Russel et al. [71]. However, from the experimental results in this work, the observed structure of NdAlO_3 was in agreement with Russell's prediction on the structure of PuAlO_3 , which is a rhombohedral structure with R-3c space group.

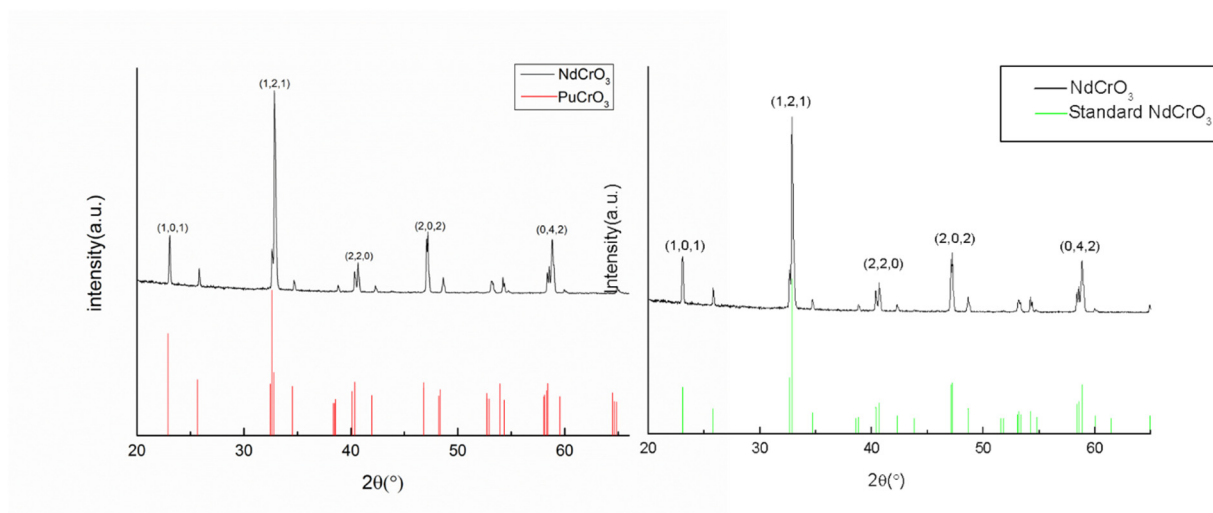


Figure 21. Indexed X-ray diffraction pattern of NdCrO_3 , with standard patterns for PuCrO_3 and NdCrO_3 shown below.

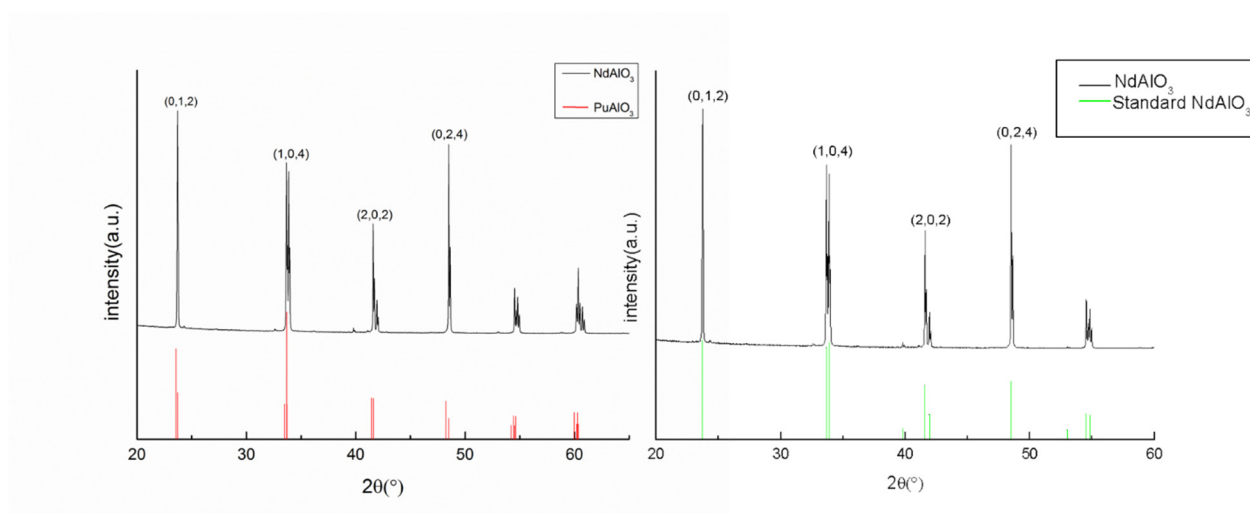


Figure 22. Indexed X-ray diffraction pattern of NdAlO_3 , with standard patterns for PuAlO_3 and NdAlO_3 shown below.

4.2.2 Scanning electron microscopy (SEM)

Figure 23 and 24 present the scanning electron microscopy (SEM) of NdCrO_3 and NdAlO_3 that were sintered to 1600°C . The back scattered electron image (**Figure 23**) shows that NdCrO_3 is single phase with no other phases observed. The black areas in **Figure 23** are pores that indicate the NdCrO_3 sample is porous.

As for NdAlO_3 , it is clear from **Figure 24** that it is single phase with no other impurities observed and it is reasonably dense with fewer pores than that for the NdCrO_3 sample.

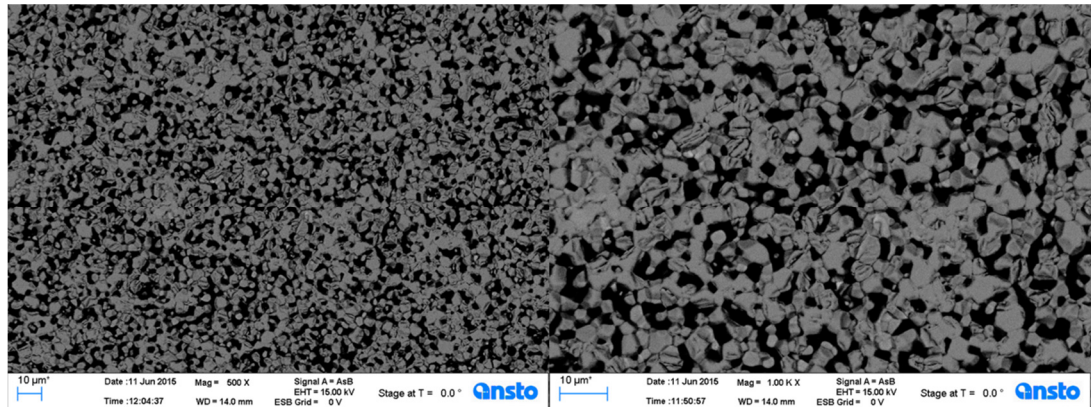


Figure 23. Scanning electron micrograph of NdCrO_3 sintered for 26h at 1600°C with 500 X and 1000 X magnification. The black areas are pores.

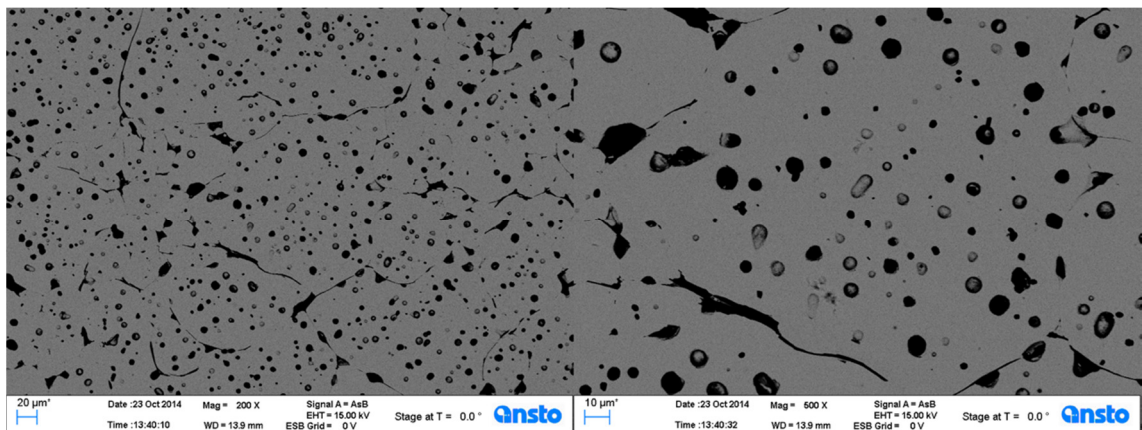


Figure 24. Scanning electron micrograph of NdAlO_3 sintered for 26h at 1600°C with 200 X and 500 X magnification. The black areas are pores and cracks.

4.2.3 Density measurement

Density was measured for these two materials using Archimedes' principle. The table below (**Table 4**) shows the bulk density, theoretical density and apparent porosity of neodymium chromate and neodymium aluminate. The bulk density that measured for NdCrO_3 is only 5.4 g/cm^3 with about 23% apparent porosity and the bulk density is 77% of theoretical density. While for NdAlO_3 , the bulk density was 6.4 g/cm^3 with 1% apparent porosity and the bulk density was almost 93% of the theoretical density. The bulk density and apparent porosity that was measured with Archimede's Principle are in well agreement with SEM results for NdCrO_3 and NdAlO_3 with regard to porosity in the samples.

Table 4. Bulk density measured with Archimedes' Principle and theoretical density of NdCrO_3 and NdAlO_3 .

Sample	Theoretical Density(g/cm^3)	Bulk Density(g/cm^3)	Apparent Porosity (%)	% of theoretical
NdCrO_3	7.09	5.44	23.01	76.71
NdAlO_3	6.91	6.41	1.03	92.87

4.2.4 Raman analysis

Raman analysis was performed on the polished pristine materials and the Raman spectra are presented in **Figure 25**.

The Spectra in black line in **Figure 25** is the Raman spectra of pristine NdCrO_3 . According to the group theory, the orthorhombic Pnma structure gives rise to 24 Raman-active modes: $7A_g + 5B_{1g} + 7B_{2g} + 5B_{3g}$. These 24 Raman active modes can be

classified into two symmetric and four asymmetric stretching modes, four bending modes and six rotation and tilt modes of the octahedra [72]. In **Figure 25**, at least 9 Raman active modes could be identified for the pristine sample; Namely: 150 cm^{-1} (A_g), 168 cm^{-1} (B_{2g}), 212 cm^{-1} (A_g), 288 cm^{-1} (B_{1g}), 335 cm^{-1} (A_g), 374 cm^{-1} (B_{1g}), 435 cm^{-1} (B_{1g}), 452 cm^{-1} (A_g), 577 cm^{-1} (B_{3g}). The main atomic motions to the nine modes are assigned to the Nd-O stretching [150 cm^{-1} (A_g)], CrO_6 bending [212 cm^{-1} (A_g)], CrO_6 stretching [288 cm^{-1} (B_{1g})], CrO_6 rotation [452 cm^{-1} (A_g)] [73]. Modes related to bending and stretching of Cr-O bonds within the octahedra appeared at the high frequency end of the spectra. Particularly, the anti-stretching vibration of the Cr-O bonds inside the octahedra is important as its frequency is very sensitive to the changes in Cr-O bond lengths [74]. The Raman result is similar with previous results from the literature [75].

Similarly for pristine NdAlO_3 , surface Raman spectroscopy was undertaken and presented in red line in **Figure 25**. At least 8 Raman active modes could be observed; namely: 162.7 cm^{-1} (E_g), 239.9 cm^{-1} (A_{1g}), 321.3 cm^{-1} , 376.4 cm^{-1} , 434.5 cm^{-1} , 453.3 cm^{-1} , 508.5 cm^{-1} (E_g), 553.6 cm^{-1} . According to the group theory, the rhombohedral structures give rise to 5 Raman-active modes: $A_{1g} + 4E_g$ [76]. For Rhombohedral structure, the Raman spectra can be divided into $1A_g + 1E_g$ – rotational or tilt modes, $1E_g$ - bending, and $1E_g$ anti-stretching of the AlO_6 octahedra, and the remaining E_g is related to a vibration of Nd ions [77].

Among these 8 bands as shown in **Figure 25**, there are three major bands, centred at 162.7 cm^{-1} , 239.9 cm^{-1} and 508.5 cm^{-1} . The band at 162.7 cm^{-1} can be assigned to the motion of Nd^{3+} ions. A_{1g} mode at 249 cm^{-1} is due to the rotation of the AlO_6 octahedra. The 508.5 cm^{-1} band mainly results from the bending of the AlO_6 octahedra. The other bands that range from 300 to 480 cm^{-1} and from 550 and 700 cm^{-1} are connected to the

vibrations of the Nd^{3+} ions in their own sites and those vibrations that involve the Nd^{3+} ions [78]. This Raman spectra for NdAlO_3 is in good agreement with the results previously reported for NdAlO_3 [78].

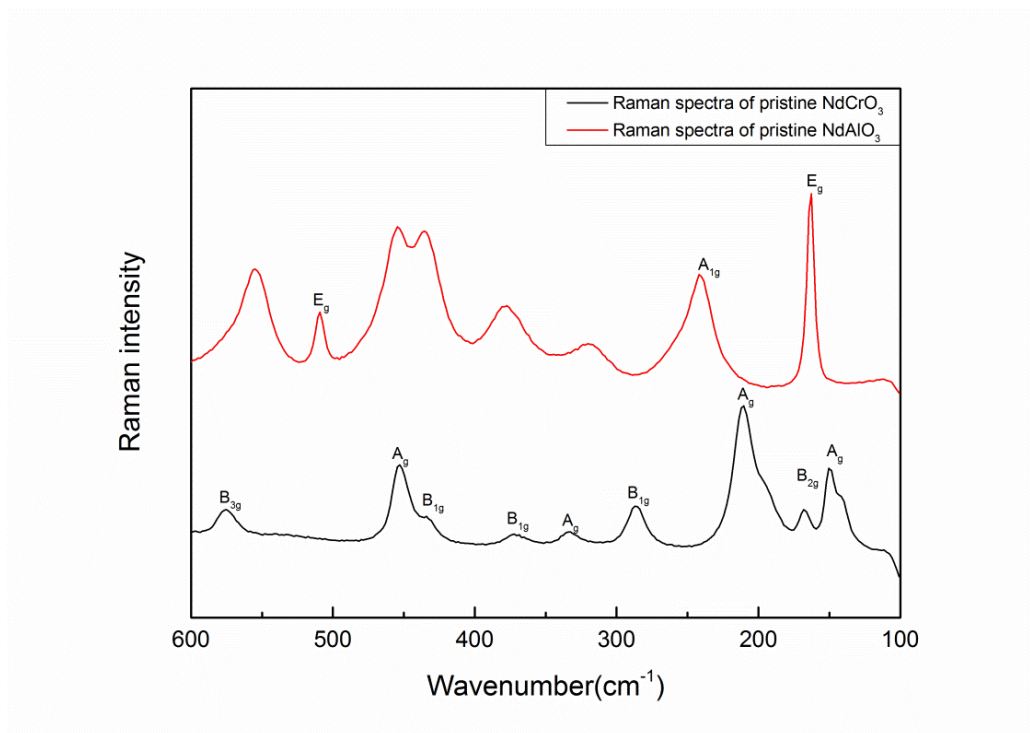


Figure 25. Raman spectra for polished pristine NdCrO_3 and NdAlO_3 samples.

4.3 Conclusion

In this chapter, NdCrO_3 and NdAlO_3 polished material has been characterized using X-ray diffraction (XRD), scanning electron microscopy (SEM) and Raman spectroscopy, and samples density was determined.

Combining the results of XRD, SEM, surface Raman and density measurements; it is concluded that NdCrO_3 is single phase, porous material with 23% porosity and exhibits the orthorhombic $Pnma$ structure. Further, SEM is in agreement with the measured

porosity. All results are in well agreement with previous results reported in literature for NdCrO_3 .

Similarly, the NdAlO_3 sample is single-phase material with rhombohedral R-3c structure. The reduced amount of pores seen in SEM is in agreement with the measured porosity (1%) and Raman spectra concur with previous results of NdAlO_3 .

Chapter 5 Thermophysical Properties of NdCrO₃ and NdAlO₃

5.1 Introduction

Thermophysical properties mean the response of a material to the application of heat. When a solid absorbs heat, its temperature will rise as well as its dimensions. If temperature gradients exist, the heat may be transported to cooler regions of the specimen, and eventually, the sample may melt. Thermophysical properties may vary with state variables like temperature, pressure and composition and of other relevant variables without changing the chemical properties of material. Heat capacity, thermal expansion and thermal diffusivity are often determined factors to assess the thermophysical properties of materials.

In this project, to understand the thermal properties of neodymium chromate and neodymium aluminate, three parameters are required: heat capacity (C_p), bulk density (ρ) and thermal diffusivity (α). Then, with the formula $[K = \alpha \cdot \rho \cdot C_p]$, the thermal conductivity could be calculated and compared with UO₂ fuel from literature. Three instruments were used to measure these parameters; STA 449 F1 Jupiter (Netzsch, Germany) was used to measure the specific heat capacity of the material. DIL 402C (Netzsch, Germany) measured the thermal expansion of the material and the LFA 467 HT (Netzsch, Germany) was utilized to measure thermal diffusivity.

5.2 Results and Discussion

5.2.1 Heat Capacity(C_p)

To measure the heat capacity, a pelletized sample and reference (sapphire) were required. Three runs were required (Baseline, reference and sample) in a measurement and the specific heat capacity was calculated by ratio method based on baseline, reference and sample measurements. **Figure 26** contains the heat capacity data of NdCrO_3 and NdAlO_3 and the heat capacity of each sample was plotted using dotted red/black line.

The tendency of heat capacity of NdAlO_3 and NdCrO_3 is almost the same and the heat capacity of both materials increased as expected from Debye theory. Comparing both materials, NdAlO_3 maintains higher heat capacity than that of NdCrO_3 within this temperature range. When the temperature was heating from 50°C to 900°C , heat capacity of NdCrO_3 and NdAlO_3 gradually increased to around 0.55 and $0.59 \text{ J}/(\text{g}\cdot\text{K})$, respectively. Thereafter, the heat capacity of NdAlO_3 shows a slight decrease and finally stabilises at $0.58 \text{ J}/(\text{g}\cdot\text{K})$ and that of NdCrO_3 is stable at $0.55 \text{ J}/(\text{g}\cdot\text{K})$.

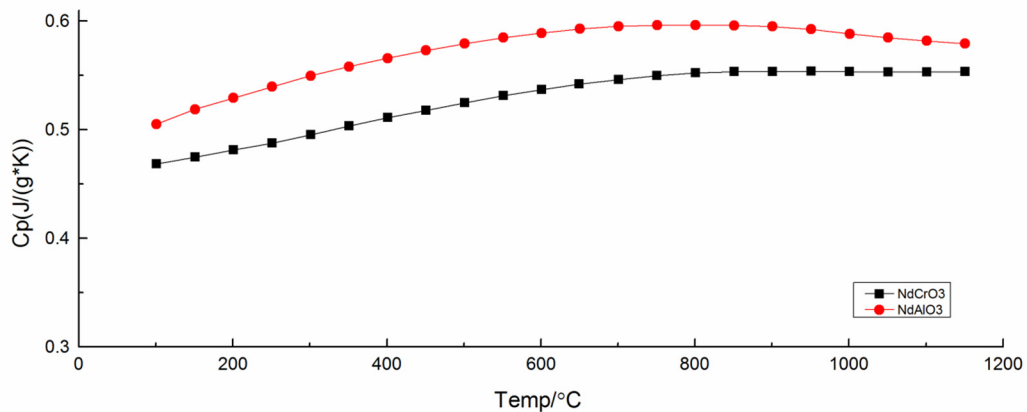


Figure 26. Temperature dependence of heat capacity of NdAlO_3 and NdCrO_3 heating to 1100°C .

5.2.2 Thermal expansion

Thermal expansion is the tendency of matter to change in volume with a change in temperature, through heat transfer. The linear thermal expansion coefficient of NdCrO_3 and NdAlO_3 are presented in **Figure 27**.

As can be seen in **Figure 27**, the thermal expansion behaviour in these systems is relatively normal, and the measured thermal expansion of both samples is linear across the temperature range of interest. (dL/L_0) increases with the increase of temperature. The linear thermal expansion coefficient for NdAlO_3 and NdCrO_3 are $1.13 \times 10^{-5} \text{ K}^{-1}$ and $9.58 \times 10^{-6} \text{ K}^{-1}$, respectively. It could be found that variation of thermal expansion of these two materials are not evident, as thermal expansion is a mechanical process where the grains expand with increasing temperature; therefore, there is no phase change or chemical reaction during heating. Comparing the linear thermal expansion of NdCrO_3 with that of NdAlO_3 , NdAlO_3 shows a higher linear thermal expansion than that of NdCrO_3 when the temperature is beyond 700°C .

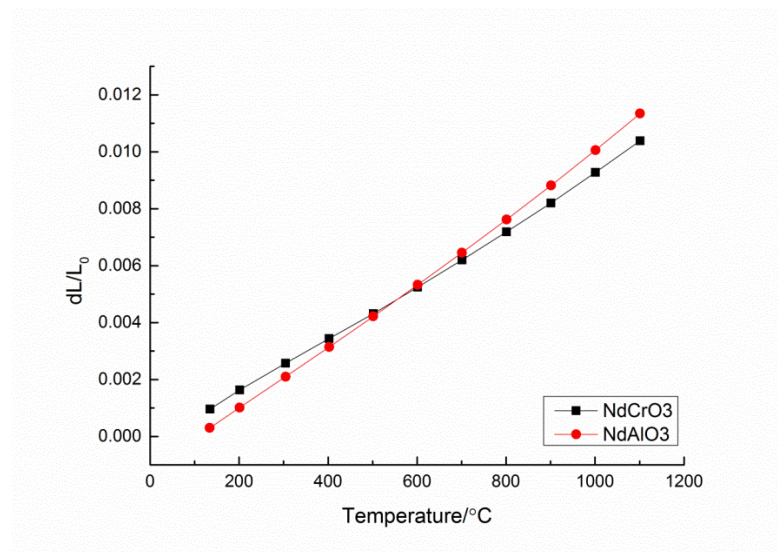


Figure 27. Temperature dependency of thermal expansion of NdCrO_3 and NdAlO_3 heating to 1100°C .

5.2.3 Thermal diffusivity

Thermal diffusivity is expressed as the thermal conductivity divided by the product of specific heat capacity and density. It is a measure of the ability of a material to transmit a difference in temperature. The thermal diffusivity data obtained for the NdCrO₃ and NdAlO₃ are shown in **Figure 28**. Both samples show the same trend and the thermal diffusivity decreased from room temperature to 1100°C. This decrease is typical for phonon conductors ($\propto 1/T$). It is clear from **Figure 28** that NdAlO₃ possesses higher thermal diffusivity than that of NdCrO₃ at this temperature range; and at the temperature of 1100°C, the thermal diffusivity of NdCrO₃ and NdAlO₃ are 0.6 and 0.9 mm²/s, respectively.

When compared these three parameters (heat capacity, thermal expansion and thermal diffusivity) with those of UO₂ from literature (**Table 5**), it is found that at the temperature of 1100°C, they have the similar heat capacity and thermal expansion among NdCrO₃, NdAlO₃ and UO₂. Thermal diffusivity is the factor that may cause the difference among them [79-81].

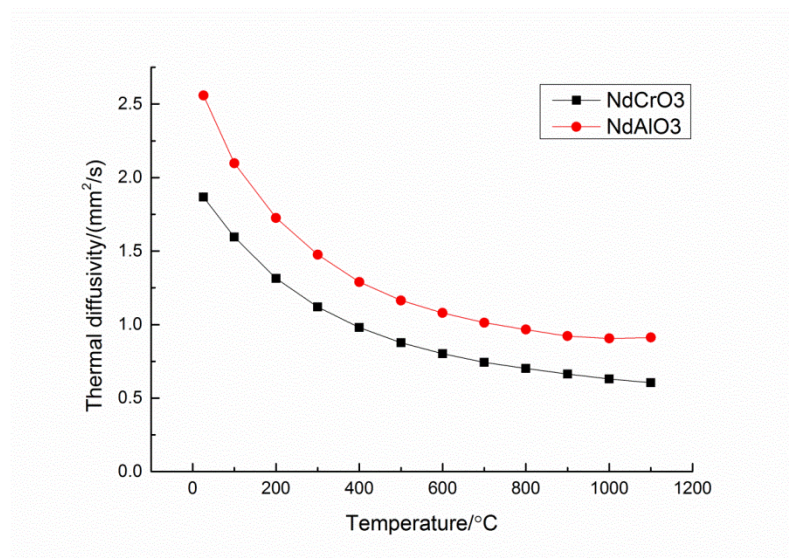


Figure 28. Temperature dependence of thermal diffusivity of NdCrO₃ and NdAlO₃ heating to 1100°C.

Table 5. Comparison of specific heat capacity, thermal expansion and thermal diffusivity among NdCrO₃, NdAlO₃ and UO₂ (from literature) at 1100°C [80-82].

	Specific heat (C _p) (J/g·K ⁻¹)	Thermal expansion (K ⁻¹)	Thermal diffusivity (mm ² /s)	Thermal conductivity (W/mK)
NdCrO ₃	0.59	9.58×10^{-6}	0.6	2
NdAlO ₃	0.55	10.13×10^{-6}	0.9	4
UO ₂	0.40	10.47×10^{-6}	0.8	2.5

5.2.4 Thermal conductivity

Thermal conductivities of NdCrO₃ and NdAlO₃ were calculated as the product of the thermal diffusivity (α), specific heat capacity (C_p) and bulk density (ρ) that was measured using Archimedes' method. The calculated thermal conductivities for both materials are displayed in **Figure 29**, and the resulting thermal conductivity of each sample decreases between room temperature and 1100°C. The thermal conductivities of NdCrO₃ and NdAlO₃ are approximately 2 and 4 W/mK at 1100°C. NdAlO₃ (Rhombohedral R-3c structure) holds much higher thermal conductivity than that of NdCrO₃ (Orthorhombic Pnma structure). This concurs with the results for PuCrO₃ and PuAlO₃ that were obtained through computational methods (Chapter 2, Figure 7) [6]. However, limited data exist on the thermophysical properties of NdCrO₃ and NdAlO₃, therefore it is not possible to provide comparison data for the measured values reported here.

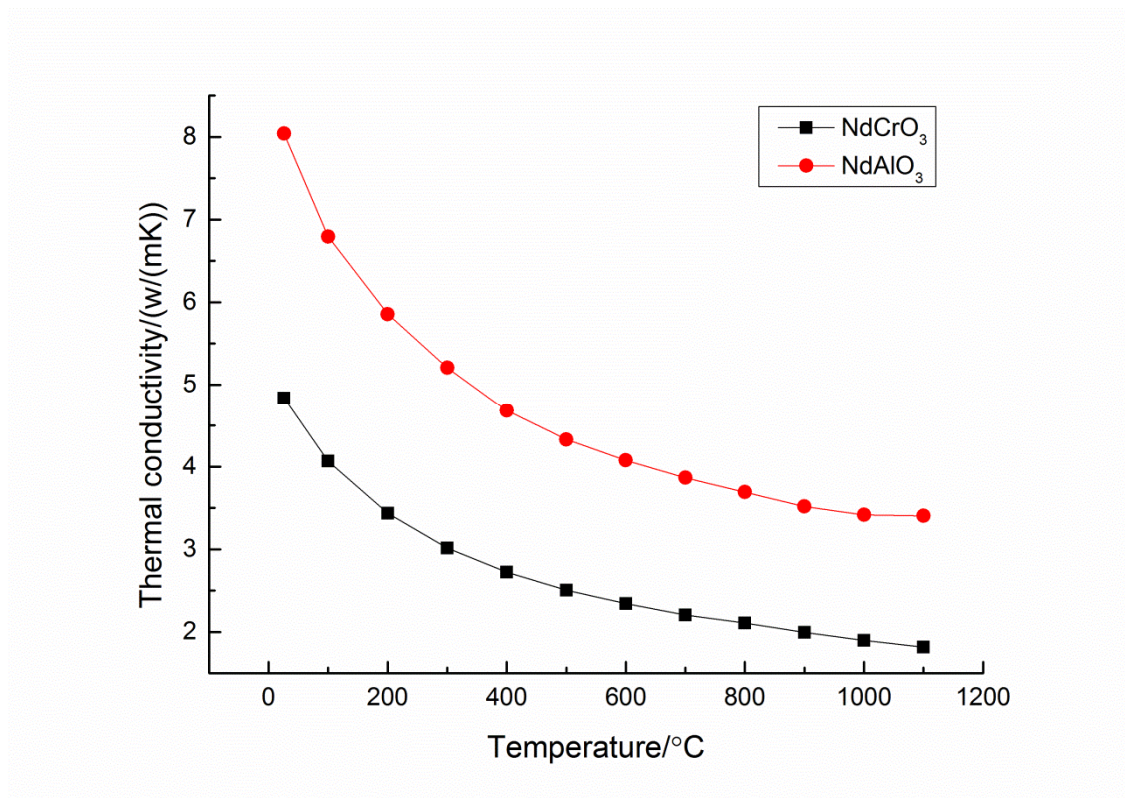


Figure 29. Temperature dependence of thermal conductivity of NdCrO₃ and NdAlO₃.

Table 6 lists the thermal conductivities of different samples (NdCrO₃, NdAlO₃, PuCrO₃, PuAlO₃ and UO₂) at temperatures of 400 and 1100°C. All the samples (through both computational method and experimental method) show downward trends of thermal conductivity between 400 and 1100°C. However, It can be seen that there is an overall difference of thermal conductivity between Nd compounds and Pu compounds. It is expected to influence the thermal conductivity results, but without further work, more explanations cannot be provided. Therefore, the general trend rather than the exact data can be compared only. Further, the calculation of thermal conductivities of NdCrO₃ and NdAlO₃ through computational method would provide a better comparison.

Table 6. Thermal conductivities of different samples at the temperatures of 400 and 1100 °C. Data of PuCrO₃, PuAlO₃ and UO₂ through computational method is from literature by Fullarton, data of UO₂ through experimental result is from literature by Pillai [82].

Sample	Thermal conductivity at 400°C (W/mK)	Thermal conductivity at 1100°C (W/mK)
NdCrO ₃	3	2
NdAlO ₃	5	4
PuCrO ₃ (computational method)	4	3
PuAlO ₃ (computational method)	9	7
UO ₂ (computational method)	11	6.5
UO ₂ (experimental method)	4.5	2.5

According to Fullarton et al [6], The thermal conductivities of PuCrO₃ and PuAlO₃ through computational method are about 3 and 7 W/mk at 1100°C (Chapter 2, Figure 7). The predicted thermal conductivity of UO₂ is about 6.5 W/mK that was found to be ~3 times greater than that of PuCrO₃ within the temperature. The thermal conductivity of UO₂ from experimental measurement through literature [82, 83] was found to be around 2.5 W/mK at 1100°C. Comparing measured thermal conductivity of UO₂ with NdCrO₃, and NdAlO₃, it can be seen that UO₂ had higher thermal conductivity than that of NdCrO₃ within the temperature range, while it has lower thermal conductivity than that of NdAlO₃. This is in good agreement with the computational method due to the same trend is observed. Therefore, as Nd was selected as the surrogate of Pu, it could be concluded that PuCrO₃ has lower thermal conductivity than that of UO₂ and PuAlO₃ has higher thermal conductivity than that of UO₂. This is similar to that predicted from computational methods.

At elevated temperature, the thermal conductivity of PuAlO₃ showed higher thermal conductivity than that of UO₂ fuel meaning the thermal impact that this oxide has on the fuel is lower. In contrast, PuCrO₃ has lower thermal conductivity than that of UO₂ fuel. Decreases in thermal conductivity of a pellet will have implications on the thermal

behavior of Cr-doped fuels and will lead to microstructural or macroscopic change. A similar example was provided by Arborelius et al. [84], which showed a comparison between a doped fuel and a standard UO_2 fuel and its notable structure differences between standard fuel pellets and doped pellets after irradiation. Actually, the doped fuel can develop a center line hole surrounded by columnar grains and this indicates the restructuring of the material [6]. Decreases in thermal conductivity of a pellet will cause an increasing centerline pellet temperature. As mentioned before, as decrease in thermal conductivity of a pellet will affect the thermal behavior of UO_2 fuels and therefore will have knock-on effects on the gas release properties, structure and fission product accommodation. As for the gas release properties, the enhanced fuel temperatures, which may be caused by lower thermal conductivity, may further increase fission gas release and this may increase the rod internal pressure. This can lead to microstructural evolution and/or a change in fracture behaviour. In terms of safety, if radioactive gases are released from UO_2 to the free volume of fuel rod, it may decrease the safety margin of a nuclear plant. Therefore, it is clear from the work that the presence of PuCrO_3 and PuAlO_3 in UO_2 fuel may have significant effect on the thermal behavior of UO_2 fuel.

5.3 Conclusions

In this chapter, neodymium chromate and neodymium aluminate samples were prepared for heat capacity, thermal expansion and thermal diffusivity measurements and the data used to calculate the thermal conductivities for both materials.

The results indicate that heat capacity, density and thermal diffusivity of NdAlO_3 are higher than those of NdCrO_3 ; therefore, the thermal conductivity, as a product of these parameters, shows higher values than that of NdCrO_3 . Comparing thermal conductivities of both NdCrO_3 and NdAlO_3 with the measured thermal conductivity of UO_2 from literature, it is found that NdCrO_3 had lower thermal conductivity and NdAlO_3 possesses higher thermal conductivity than that of UO_2 . The presence of these phases in UO_2 fuel may have impact on the thermal behavior of UO_2 fuel and microstructural or macroscopic changes could be observed.

Chapter 6

Ion beam irradiation and Characterization on irradiated NdCrO₃ & NdAlO₃

6.1 Introduction

Ion beam irradiation has become a significant application to simulate radiation damage in recent years. Specifically, ion beam irradiation is capable of easily controlling temperature, energy and fluence. Ion beam irradiation has the potential to save time and money and ion beam simulation allows easy variation of the irradiation parameters like dose, dose rate and temperatures over a wide range of values.

In this chapter, in order to investigate and understand the radiation tolerance of NdCrO₃ and NdAlO₃ which are used as the surrogate for PuCrO₃ and PuAlO₃, two sets of ion irradiations (using Au & He ions) were carried out on NdCrO₃ and NdAlO₃ at different fluences. This is followed by characterization using grazing incidence x-ray diffraction (GI-XRD), Nano-indentation, cross-sectional Raman and cross-sectional SEM. Annealing of the damaged material is another important quality to be investigated, and recrystallization of the damaged material at various temperatures was studied here.

Simulation studies using SRIM 2013 were utilized to evaluate the damage depth of the Au and He-ions in order to make a comparison with experimental results.

6.2 Results and Discussions

6.2.1 Grazing incidence X-ray diffraction

GI-XRD was only carried out on samples irradiated with Au-ions but not those irradiated with He-ions. This is because when using SRIM 2013 to calculate the damage

depth of these two materials, it was found that the damage depth of He-ion irradiation is approximately 12 to 15 μm . This damage depth would need an incident angle of more than 15° and this is impractical.

The following patterns (**Figure 30 and 33**) are the results of GI-XRD analysis on un-irradiated and 10^{13} , 10^{14} and 10^{15} Au- ions/ cm^2 irradiated NdCrO_3 and NdAlO_3 with the chosen incident angle of 5° . The reason to choose 5° as incident angle is that under this incident angle, the calculated penetration depth of the x-rays is around 0.7 μm for NdCrO_3 and NdAlO_3 , most similar to the damaged depth (1.46 μm) as indicated by SRIM 2013 calculations.

NdCrO_3 - Different fluence, same incident angle (5°)

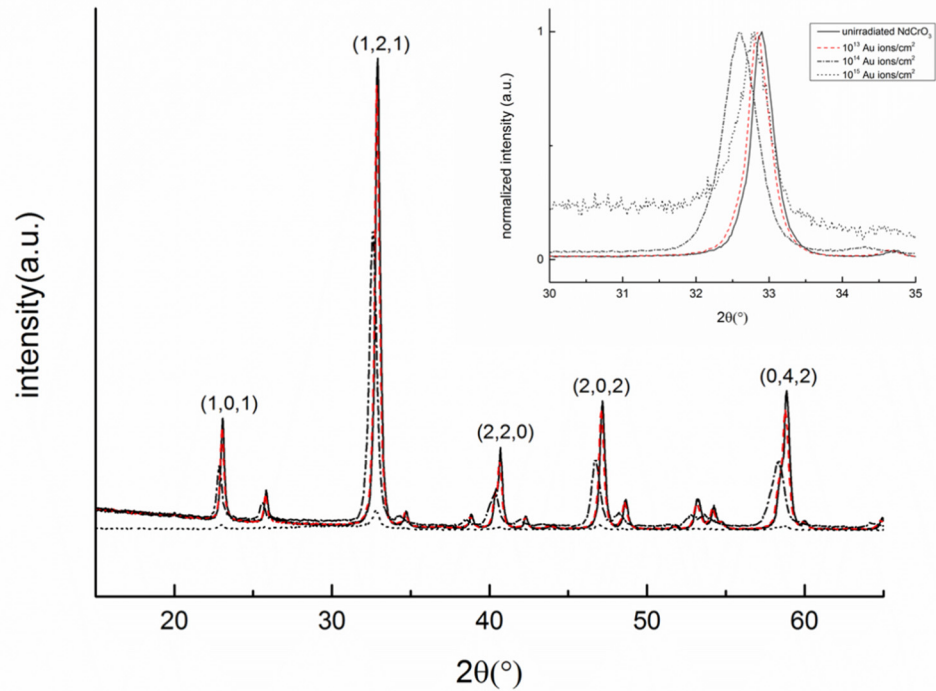


Figure 30. GI-XRD pattern using a 5° incidence angle for (—) un-irradiated, (— —) 10^{13} , (— ·) 10^{14} and (··) 10^{15} Au-ions/ cm^2 irradiated NdCrO_3 .

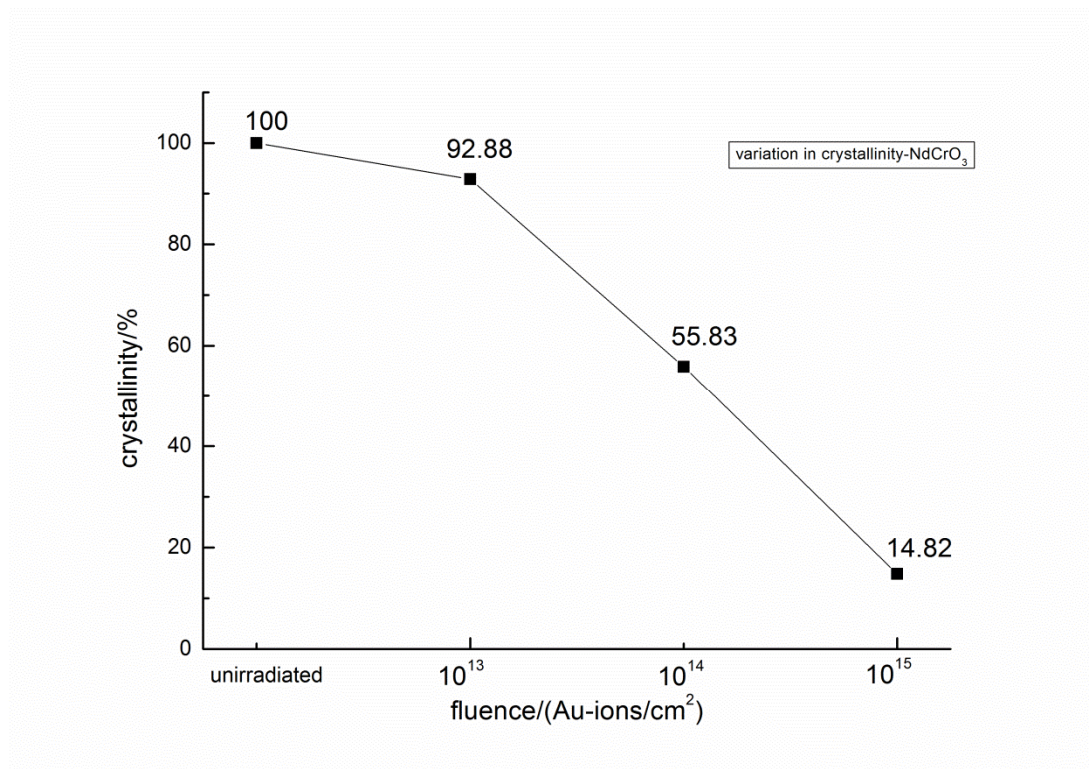


Figure 31. Variation of crystallinity of NdCrO₃ versus ion fluence.

GI-XRD patterns of pristine and irradiated NdCrO₃ are presented in **Figure 30** using an incident angle of 5°. All the samples exhibit a single orthorhombic phase. No change in phase is apparent with irradiation. The increase in Au ion fluence reduces the peaks' intensities and no extra peaks are observed. It is apparent from the GI-XRD that the pellets irradiated with Au ions at 10¹³ and 10¹⁴ ions/cm² show a slight shift of 0.2° 2θ toward lower diffraction angles together with a decrease intensity of the diffraction peaks in comparison to the virgin sample. In addition, the peaks broaden, particularly for the sample irradiated with 10¹⁴ Au-ions/cm². For the samples followed 10¹⁵ Au ions/cm² irradiation, irradiation caused nearly complete amorphization as indicated by loss of peak intensity. By comparing the intensity of each peak in the pattern of these three fluences with un-irradiated NdCrO₃'s intensity, the average variation of crystallinity (that calculated with peaks at around 23, 32, 40, 47 and 58° 2θ) is presented in **Figure 31**. This figure clearly shows that the sample irradiated with 10¹³ Au-ions has

little damage to crystallinity suggests little damage. The sample kept almost 93% crystallinity compared with the pristine sample. With the fluence increased to 10^{14} Au-ions/cm², NdCrO₃ showed significant damage with only about 55% crystallinity remaining. The sample eventually became near completely amorphous; only approximately 15% crystallinity compared with the un-irradiated one after irradiation with 10^{15} Au-ions/cm².

Besides the variation in peak intensity that could be observed directly from the patterns, the program RIETICA was employed to refine the lattice parameters with the Le Bail method. The results are summarized in **Table 7** below. The unit cell volume was calculated with the refined lattice parameters and the variation of unit cell volume as a function of ion fluence is shown in **Figure 32**. As the peaks are broader after irradiation, unit cell parameters are less accurate and the figure only provides the general trend. Therefore, **Figure 32** presents the general variation of unit cell volume follows irradiation with Au ions of different fluences. It is clear that the unit cell volume increases with the increase of Au-ion fluence. This effect is small when comparing the sample irradiated with 10^{13} Au ions/cm² and the pristine material. However, the effect is dramatic at higher fluence of 10^{14} and 10^{15} Au-ions/cm².

When the Au ion penetrates NdCrO₃, it collides with the nuclei and the electrons of the target. With the collision of Au ion, defects will appear in the target and these defects include interstitial defects and vacancies. Irradiation produces point defects and defect clusters in the material, thus the lattice shows expansion as indicated by unit cell volume increases for NdCrO₃. The higher the fluence, the more amounts of ions deposited in the sample and was server the damage; therefore, the expansion of high dose rate irradiated NdCrO₃ is much more obvious. Similar volume expansions

following Au ion beam irradiation has been demonstrated in previous work on other materials like monazite compounds [40] and gadolinium zirconate [85]. It is clear from the work that Au ion irradiation may destroy the long-range crystalline order in NdCrO₃ above a fluence of 10¹³ Au-ions/cm².

Table 7 Lattice parameter and unit cell volume of un-irradiated, 10¹³, 10¹⁴ and 10¹⁵ Au ions/cm² irradiated NdCrO₃

	A(Å)	B(Å)	C(Å)	V(Å ³)	Swelling Rate (%)
Un-irradiated NdCrO ₃	5.4845(4)	7.6935(6)	5.4242(3)	228.874(1)	
10 ¹³ ions/cm ²	5.4966(5)	7.6997(7)	5.4261(4)	229.644(1)	0.3
10 ¹⁴ ions/cm ²	5.5088(6)	7.736(1)	5.4642(6)	232.863(2)	1.7
10 ¹⁵ ions/cm ²	5.5448(5)	7.8348(7)	5.6221(4)	244.239(1)	6.7

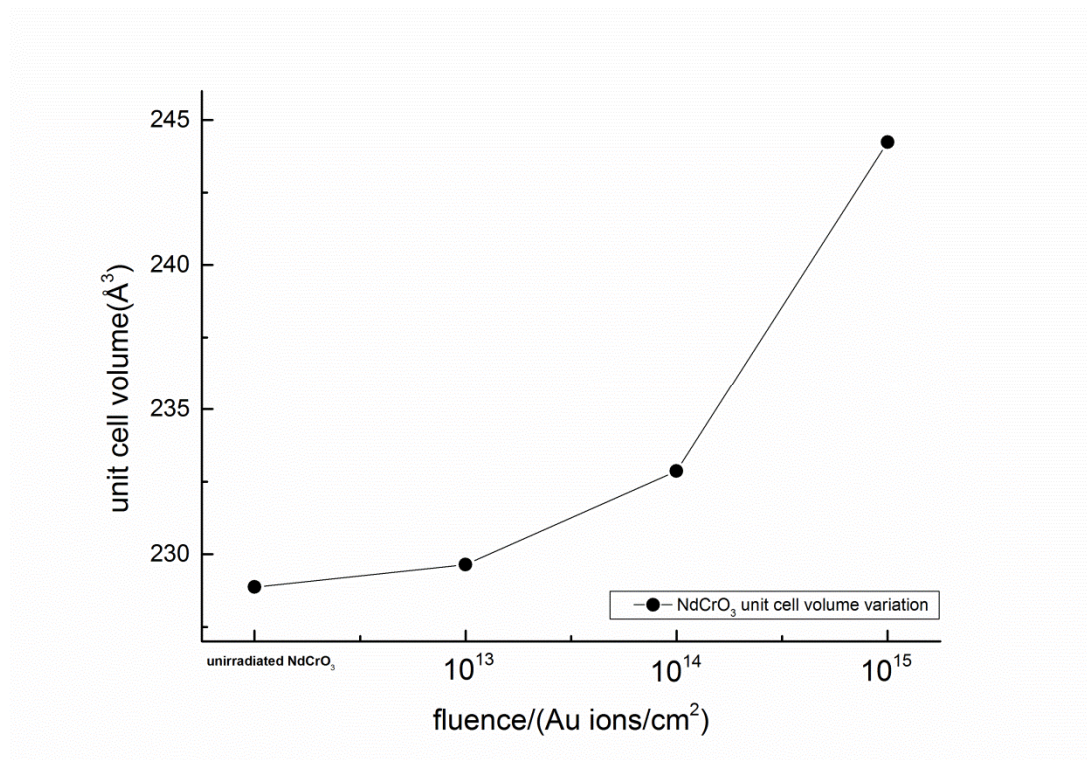


Figure 32. Unit cell volume variation versus ion fluence in NdCrO₃ irradiated with Au ions.

NdAlO₃

GI-XRD patterns for un-irradiated and 10^{13} , 10^{14} , 10^{15} Au⁺-ions/cm² irradiated NdAlO₃ are summarized in **Figure 33**. All samples exhibit single rhombohedral phase and do not show any phase change with irradiation, with no extra peaks observed following sample irradiation. It is apparent from GI-XRD that the pellets irradiated with 10^{13} and 10^{14} Au ions/cm² show a shift of 0.8° 2θ toward lower diffraction angles together with a decrease in peaks intensity when compared to the pristine NdAlO₃ sample. Similar to the NdCrO₃ sample, peaks in the GI-XRD pattern are significantly broadened following irradiation. The sample irradiated with 10^{15} Au ions/cm² is completely amorphous. It is interesting that the split peaks show up at 41.6° , 48.5° , 54.6° and 60.3° 2θ in NdAlO₃ XRD patterns that irradiated with 10^{14} Au ions/cm², and these split peaks match NdAlO₃ with hexagonal structure [86]. In this case, when NdAlO₃ irradiated with 10^{14} Au ions/cm², part of NdAlO₃ underwent the phase transition from rhombohedral to hexagonal, causing the coexistence of both phases at fluence of 10^{14} Au ions/cm². This phase conversion may be due to the tilting of AlO₆ octahedra.

When we use RIETICA to refine lattice parameters of pristine and irradiated NdAlO₃, the refinement is still general as peaks are particularly broad after irradiation, which makes it difficult to refine accurately. The variation of lattice parameters and the variation of unit cell volume as a function of ion fluence are shown in **Table 8** and **Figure 35**, respectively. It is clear that the unit cell volume shows expansion with the increase of the fluence; the sample irradiated with 10^{13} Au ions/cm² shows a slight increase in the unit cell volume which increases with increasing fluence. This unit cell expansion following Au-ion irradiation is similar to the results discussed previously for NdCrO₃ and few work published by Picot et al [40] and Wang et al [85].

As explained previously for NdCrO_3 , when Au ion penetrates NdAlO_3 , it collides with the nuclei and the electrons of the target, defects such as interstitial defects and vacancies appear. Irradiation produces point defects, defect clusters in the material, thus driving the lattice expansion at higher fluence, and the damage is more significant.

NdAlO_3 - Different fluence, same incident angle (5°)

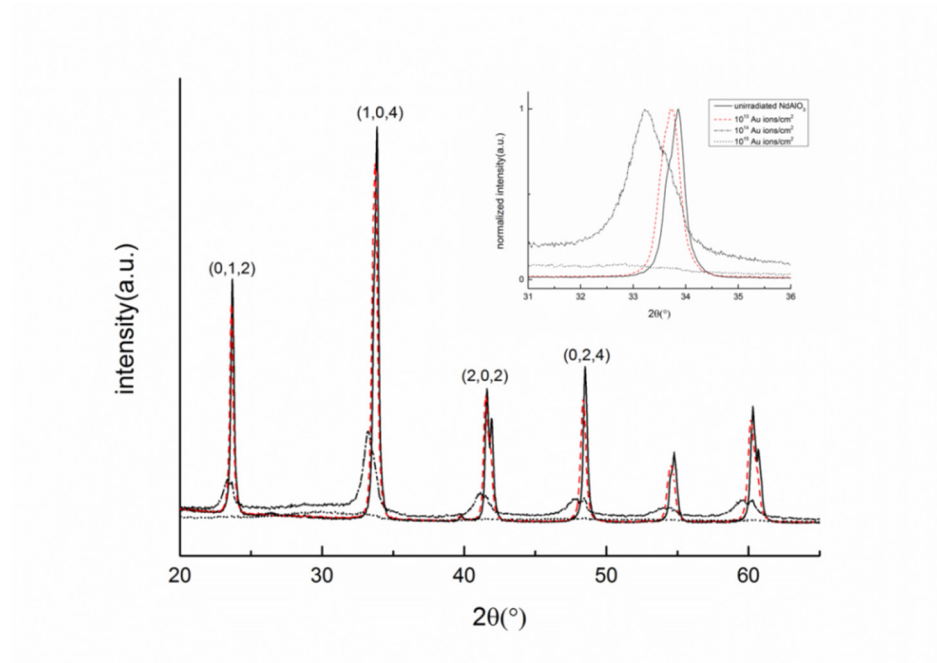


Figure 33. GI-XRD pattern using a 5° incidence angle for (—) un-irradiated, (— —) 10^{13} , (···) 10^{14} and (— ·) 10^{15} Au-ions/ cm^2 irradiated NdAlO_3

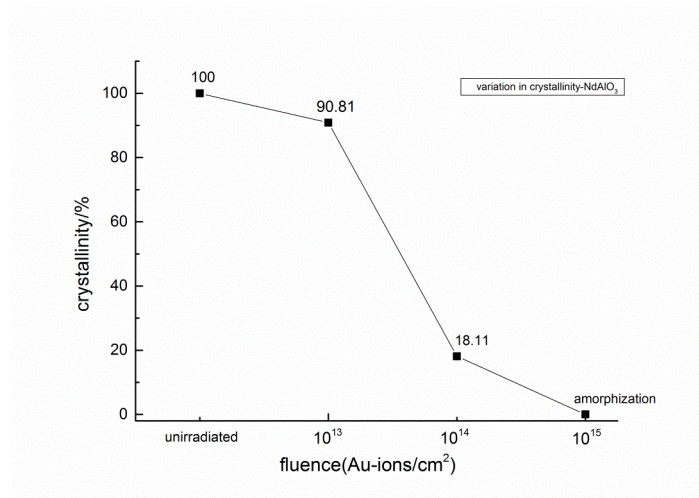


Figure 34. Variation of crystallinity of NdAlO_3 versus ion fluence.

Table 8 Lattice parameter and unit cell volume of un-irradiated, 10^{13} , 10^{14} and 10^{15} Au ions/cm² irradiated NdAlO₃

	A(Å)	B(Å)	C(Å)	V(Å ³)	Swelling Rate (%)
Un-irradiated NdAlO ₃	5.3188(7)	5.3188(7)	12.958 (2)	317.465(1)	
10^{13} ions/cm ²	5.3273(2)	5.3273(2)	12.975(1)	318.898(1)	0.5
10^{14} ions/cm ²	5.367(2)	5.367(2)	13.199(3)	329.257(7)	3.7
10^{15} ions/cm ²	5.431(1)	5.431(1)	13.494(6)	344.692(8)	8.6

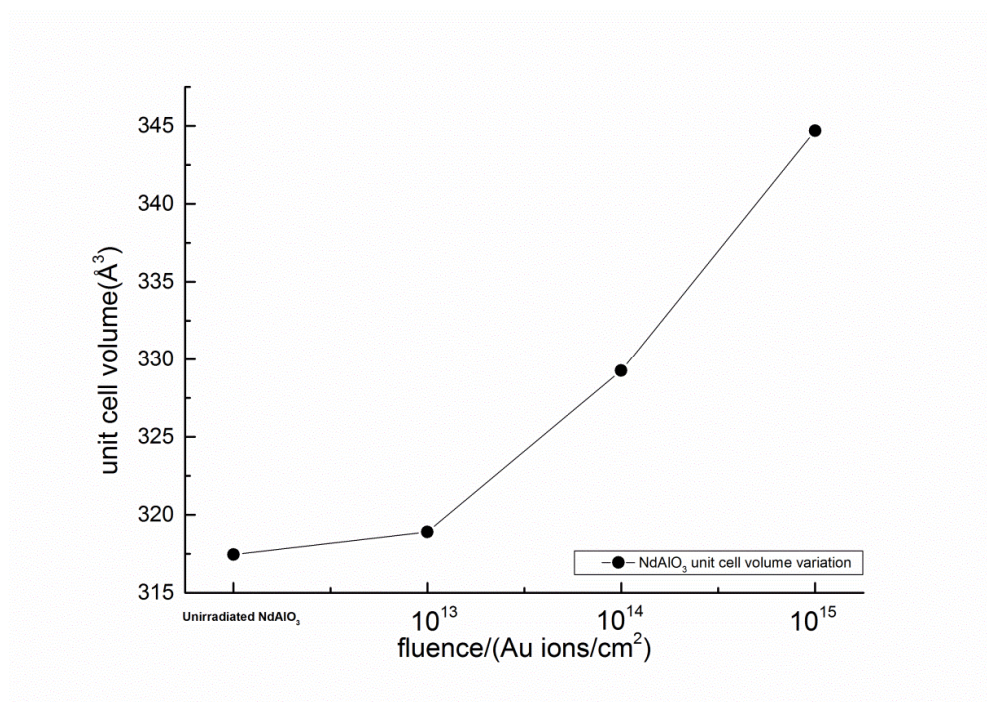


Figure 35. Unit cell volume variation versus ion fluence in NdCrO₃ irradiated with Au ions.

6.2.2 Cross-sectional SEM

The back scattered electron channelling contrast was required to observe the damage layer. The following figures present the crystallographic contrast observed following

SEM analysis of the cross-sectioned pellet followed irradiation with Au-ions at the fluence of 10^{13} , 10^{14} , 10^{15} ions/cm² and He-ions at the fluence of 10^{16} and 10^{17} ions/cm².

Cross-sectional SEM -Au ion

NdCrO₃

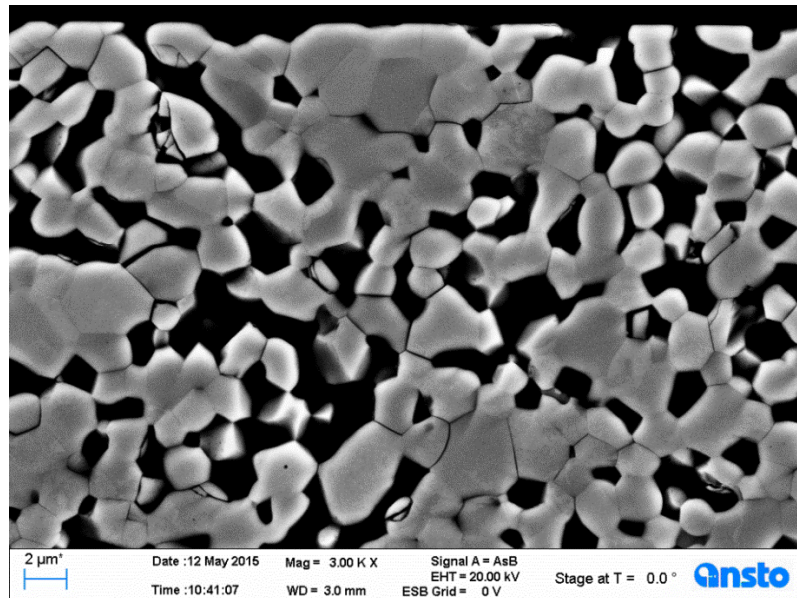


Figure 36. Crystallographic contrast observed following SEM analysis of the cross-sectioned NdCrO₃ pellet irradiated with Au-ions at the fluence of 10^{13} ions/cm².

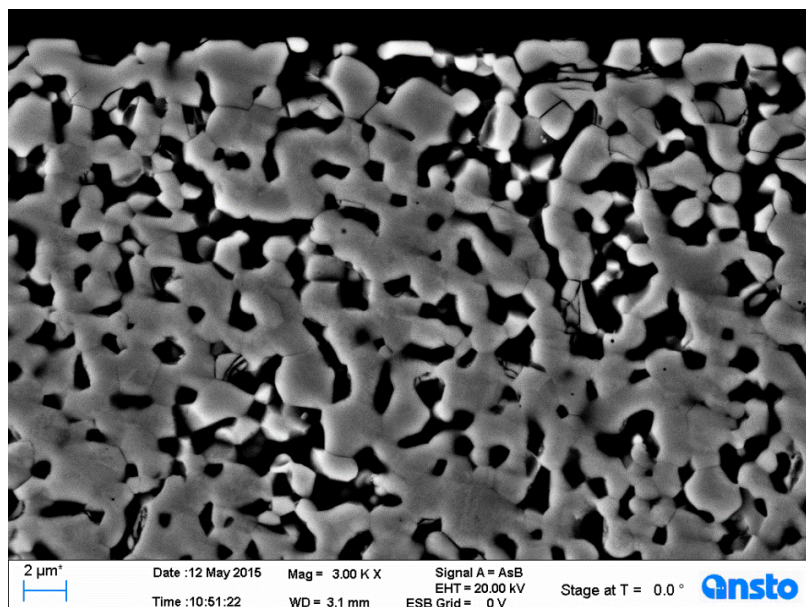


Figure 37. Crystallographic contrast observed following SEM analysis of the cross-sectioned NdCrO₃ pellet irradiated with Au-ions at the fluence of 10^{14} ions/cm².

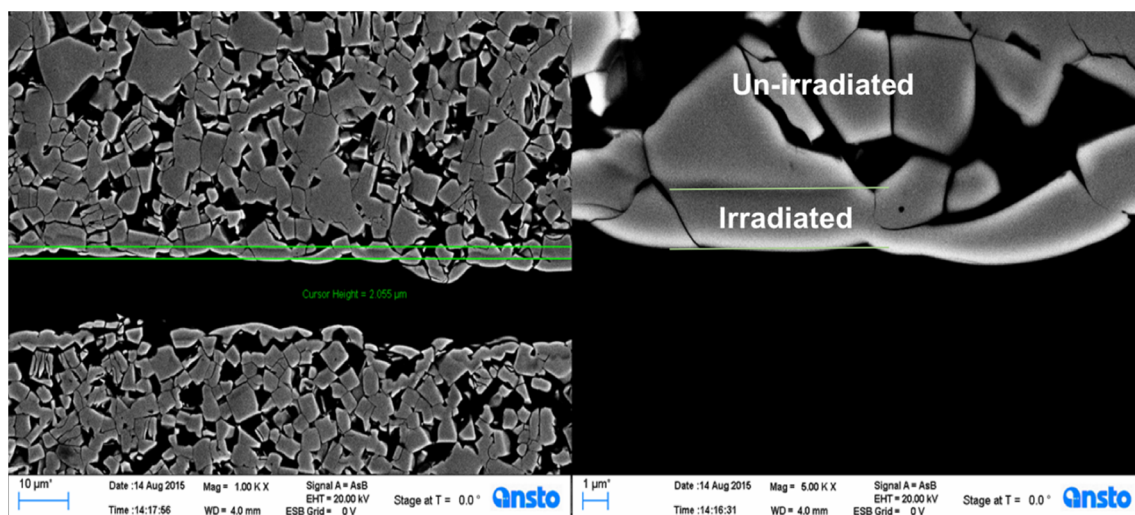


Figure 38. Crystallographic contrast observed following SEM analysis of the cross-sectioned of the NdCrO₃ pellet irradiated with Au-ions at the fluence of 10¹⁵ ions/cm².

According to the above three figures (**Figure 36, 37, 38**), no change of contrast corresponding to the damaged layer was observed for NdCrO₃ irradiated with 10¹³ and 10¹⁴ Au-ions/cm². While for material irradiated with 10¹⁵ Au-ions/cm², there is an obvious change in contrast observed in the SEM image indicating the damage layer, although this layer is not even. The uneven nature of the damage layer is due to the porosity of the material; the Au ions travel further in voids then in the solid material.

The SEM method used in this work uses a short working distance of 4 mm; using this close distance allows the observation of changes of crystallinity. For NdCrO₃ irradiated with 10¹⁵ Au-ions/cm², the damaged part is darker than the undamaged material, and the damaged layer is about 2 μm thick. For the calculated damage depth, it is 1.5 μm with ions confined within a depth of about 2.1 μm through SRIM 2013 calculation, and the measured depth is in agreement with the calculated depth. When observing 10¹³ and 10¹⁴ Au-ion/cm² irradiated NdCrO₃, it can be found that the grain morphology of these two samples are round particles, but changed to more faceted grains when NdCrO₃ followed 10¹⁵ Au-ion/cm². The possible explanation is due to the sample preparation sequence. For NdCrO₃ samples that are irradiated at 10¹³ and 10¹⁴ Au-ions/cm², they

were fabricated and irradiated simultaneously. While for NdCrO_3 sample irradiated at 10^{15} Au-ions/ cm^2 , it was prepared later. Because of different preparation time and the operator choice of specific area analysed, the grain morphology of these irradiated samples may vary and present differently from SEM figures.

Cross-sectional SEM -Au ion

NdAlO_3

Similar to NdCrO_3 , cross-sectioned SEM analysis was undertaken for NdAlO_3 .

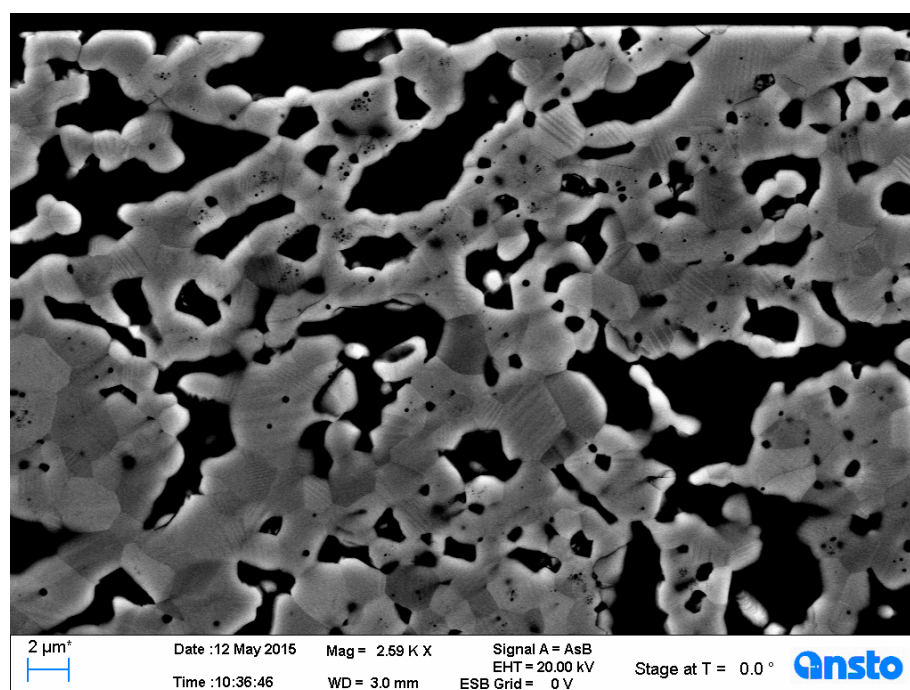


Figure 39. Crystallographic contrast observed following SEM analysis of the cross-sectioned of the NdAlO_3 pellet irradiated with Au-ions at the fluence of 10^{13} ions/ cm^2 .

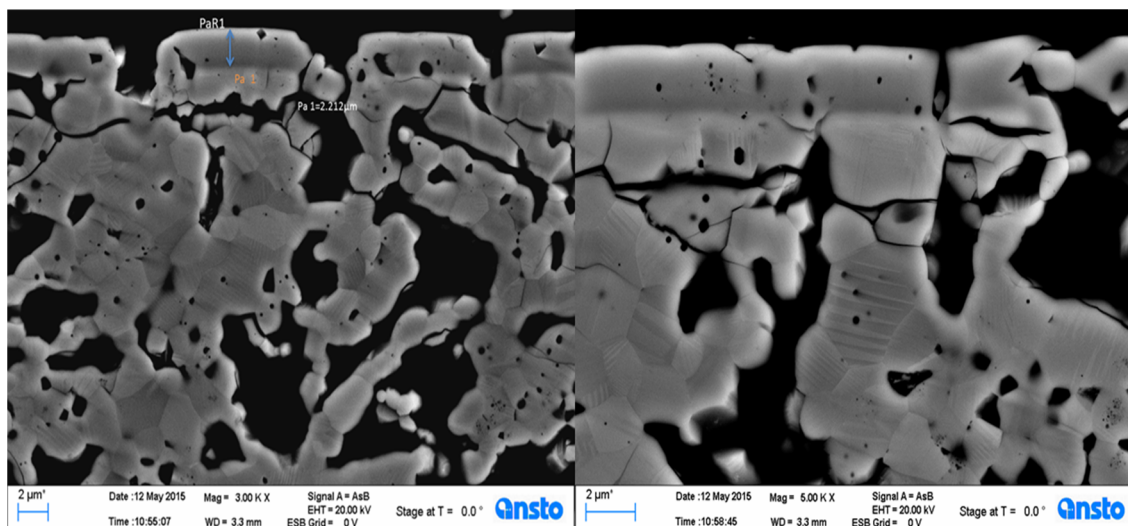


Figure 40. Crystallographic contrast observed following SEM analysis of the cross-sectioned of the NdAlO₃ pellet irradiated with Au-ions at the fluence of 10^{14} ions/cm².

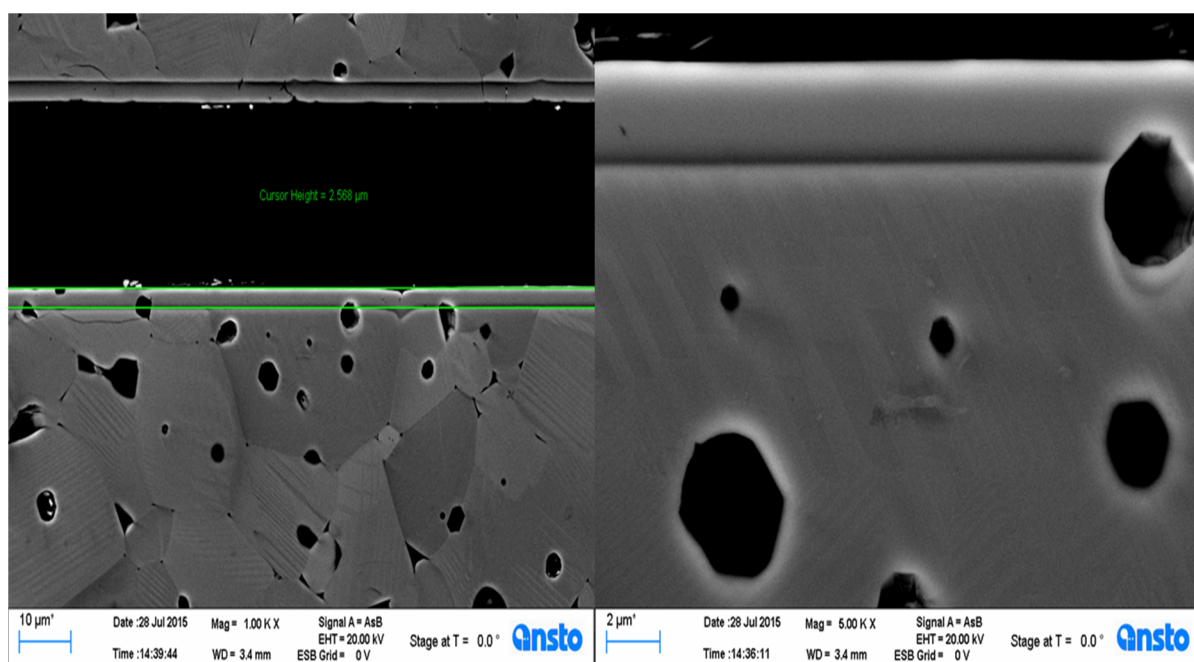


Figure 41. Crystallographic contrast observed following SEM analysis of the cross-sectioned of the NdAlO₃ pellet irradiated with Au-ions at the fluence of 10^{15} ions/cm².

For NdAlO₃, the above three figures (Figure 39, 40, 41) indicate the damage layer following different fluences. The sample irradiated with the fluence of 10^{13} Au-ions/cm², does not present a damage layer in the SEM image because of insignificant damage. However, when the fluence increases to 10^{14} Au-ions/cm², there is an obvious damage layer that could be observed from the image, the damage layer is about 2.2 μm. NdAlO₃

irradiated with 10^{15} Au-ions/cm² displays an even clearer damage layer with depth of about 2.6 μm . Through SRIM calculation, it was concluded that the peak depth was 1.8 μm with a maximum depth of about 2.2 μm . Comparing the measured and calculated results, the cross-sectional SEM agrees with the calculated result as well. Interestingly, SEM figures 39 – 41 seem to show that the pristine area of the sample irradiated with 10^{15} Au-ions/cm² is denser than the pristine areas for the samples irradiated at 10^{13} and 10^{14} Au-ions/cm². All NdAlO₃ samples were prepared simultaneously and all were CIPed. Porosity was quite variable throughout the samples and the density difference appear due to the small sample area observed in the SEM and the operator choice of specific area analysed.

Cross-sectional SEM -He ion

He-ions travel much further through the material than Au-ions. SRIM 2013 analysis suggests a peak damage depth of $\sim 15 \mu\text{m}$.

For both materials (NdCrO₃ and NdAlO₃) that irradiated with He ions (**Figure 42, 43, 44, 45**), a distinct damage layer was not observed. He ions have a range of a few tens of micrometres, and generally transferring their energy through a process of ionization and near the end of their track through elastic collisions [40].

NdCrO₃

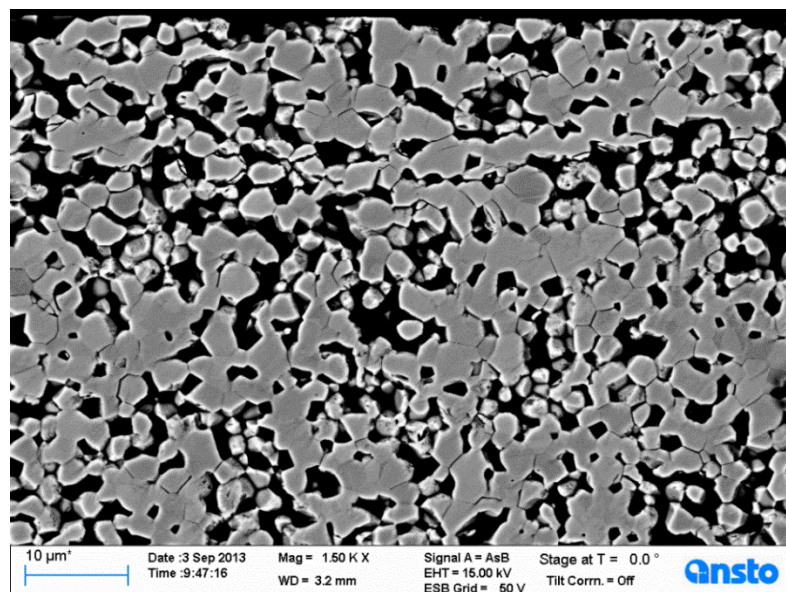


Figure 42. Crystallographic contrast observed following SEM analysis of the cross-sectioned NdCrO₃ pellet irradiated with He-ions at the fluence of 10¹⁶ ions/cm².

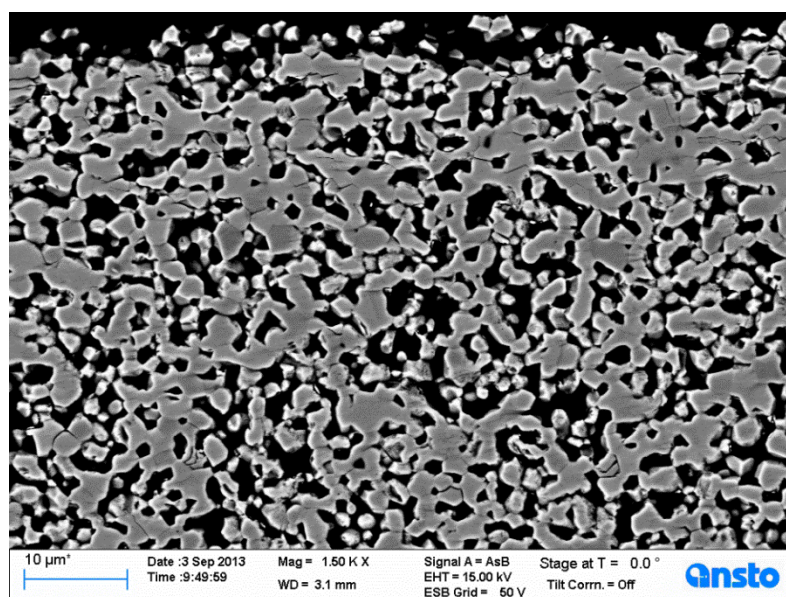


Figure 43. Crystallographic contrast observed following SEM analysis of the cross-sectioned NdCrO₃ pellet irradiated with He-ions at the fluence of 10¹⁷ ions/cm².

NdAlO₃

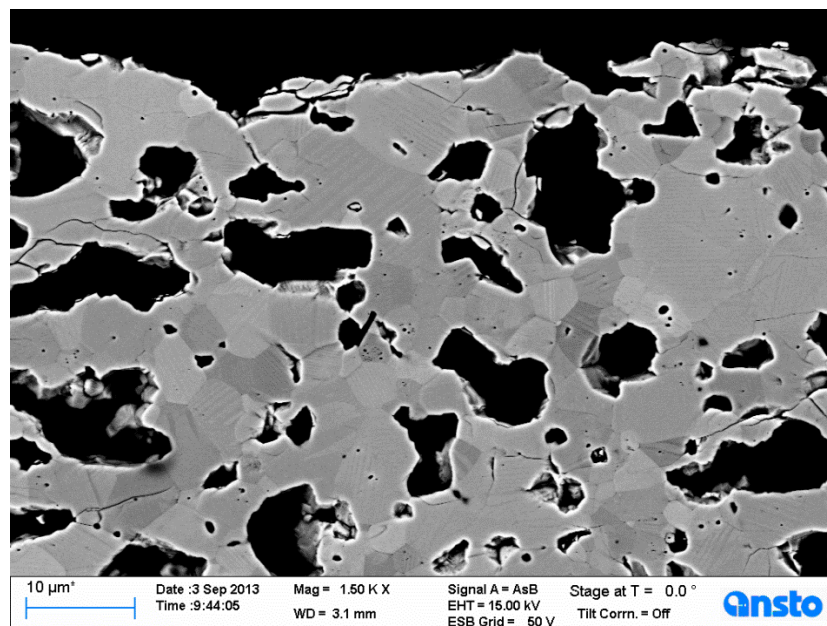


Figure 44. Crystallographic contrast observed following SEM analysis of the cross-sectioned NdAlO₃ pellet irradiated with He-ions at the fluence of 10^{16} ions/cm².

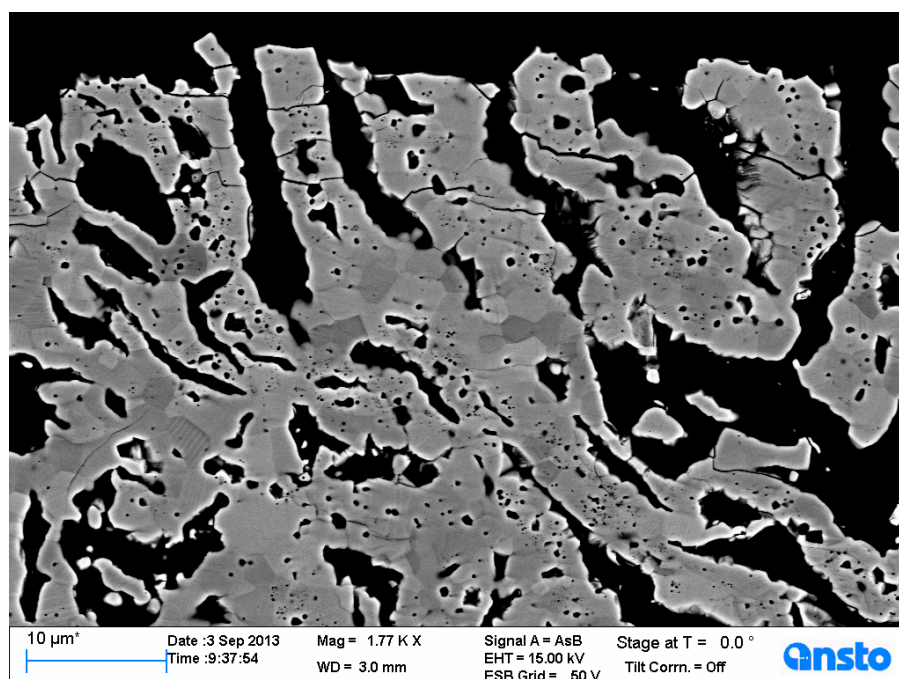


Figure 45. Crystallographic contrast observed following SEM analysis of the cross-sectioned NdAlO₃ pellet irradiated with He-ions at the fluence of 10^{17} ions/cm²

6.2.3 Cross-sectional Raman analyses

The Raman scattering technique is a vibrational molecular spectroscopy that derives from an inelastic light scattering process. Raman spectroscopy is also utilized to study the effect of ion-beam irradiation to complement the XRD analyses as it has a shorter correlation length scale of about a few unit cells. It was performed on cross-sectioned irradiated pellets at various damage depths to probe the un-irradiated and irradiated materials and observe the changes between damaged and pristine material.

- **Au ions - NdCrO₃**

Figure 46 presents the Raman spectra of the NdCrO₃ sample irradiated with 10¹⁵ Au ions/cm². The line mapping was performed from the surface and into ~ 10.5 μm depth with a step size of 1.5 μm. At depth of 9 to 10.5 μm, Raman spectra for NdCrO₃ sample are identical to the pristine material that is discussed above (Chapter 4, Figure 25) showing 9 Raman active bands. At the depth of 6 μm, Raman bands at the wavenumber of around 170, 288 and 577 cm⁻¹ show a slight broadening and the loss of Raman peak intensity. The bands are broadened and the intensity of these bands decrease further at the depth of 1.5 μm, where there is only a hump at the wavenumber of 212 cm⁻¹. Therefore, the damage is evident at the depth of 1.5 μm, which is close to the sample surface. This damage depth corresponds to the calculated depth (1.32 μm) via SRIM calculation and is in agreement with cross-sectional SEM that is about 2 μm.

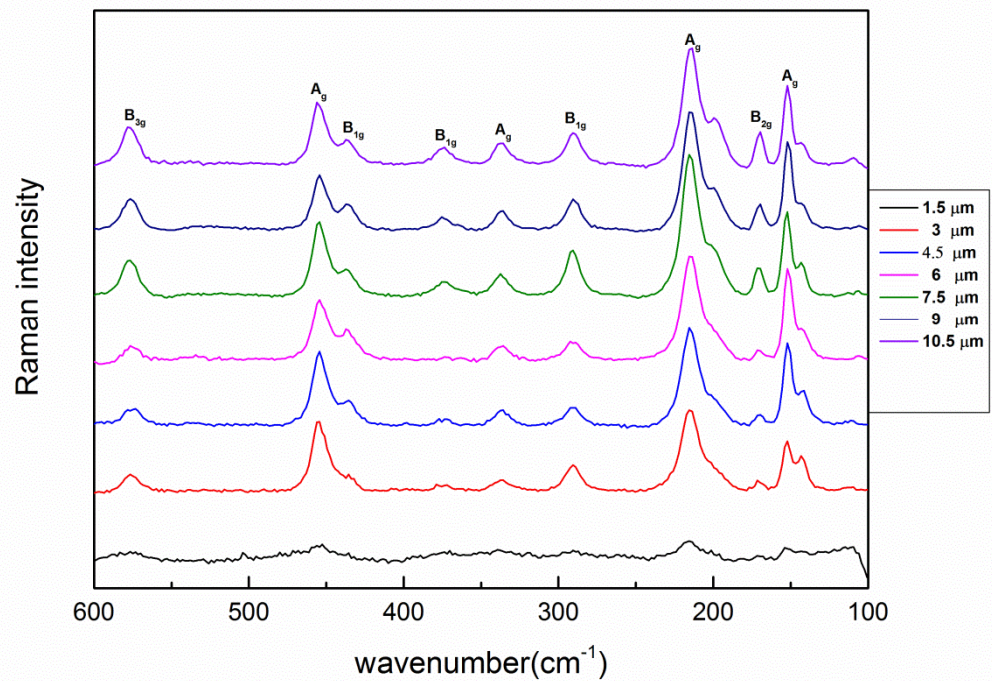


Figure 46. Raman spectra on cross-sectioned NdCrO_3 following 10^{15} Au-ions/ cm^2 irradiation.

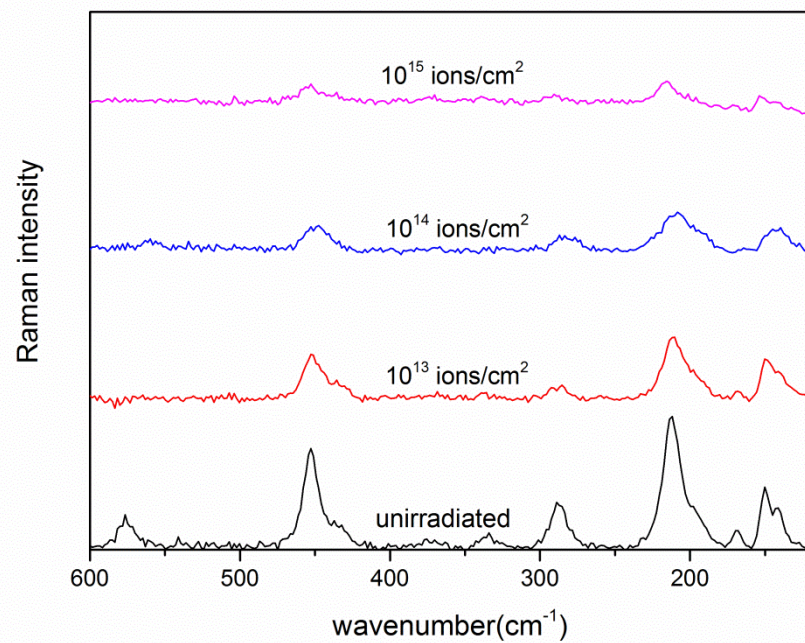


Figure 47. Raman micro-spectrometry spectra of sectioned pellets of pristine and Au-ion irradiated NdCrO_3 .

Compare samples irradiated with various fluences with the pristine sample (**Figure 47**), it is found that there are three Raman peaks (at the wavenumber of 168, 212 and 452 cm^{-1}) are still clearly visible following 10^{13} Au-ions/ cm^2 irradiation, and these bands are related to CrO_6 octahedra [73]. Other peaks that at the wavenumber of 288, 335 and 577 cm^{-1} cannot be observed after Au-ion irradiation, and they are corresponding to the Nd^{3+} ions and bending and Cr-O bonds [73, 74]. With increasing fluence, the effect is more obvious and these three left Raman bands display significant loss of peak intensity and broadening of peaks. At the highest fluence (10^{15} Au-ions/ cm^2), only a very weak peak at the wavenumber of 212 cm^{-1} , which is related to CrO_6 octahedra, is visible. Besides these changes, peak shift is found in the Raman spectra, and the remaining peaks show a slight shift (2 cm^{-1}) toward lower wavenumber from Pristine NdCrO_3 to NdCrO_3 following 10^{14} Au-ions/ cm^2 irradiation. This could be explained by Nasdala et al.[87] that the shift of the remaining bands toward lower wavenumber indicates the average distances between atoms become larger to some extent, i.e., the lattice is slightly expanded. This is in agreement with the increasing lattice parameter calculated from GI-XRD that indicates the expansion of lattice parameter. In other words, Raman bands shift toward lower wavenumber is due to the general widening of bond length [88] and this may be caused by the distortion of CrO_6 octahedra. However, at the fluence of 10^{15} Au-ions/ cm^2 , the peak at the wavenumber of 215 cm^{-1} shows a shift (3 cm^{-1}) towards higher wavenumber and this is considered as the experimental error. The broadening of Raman bands and disappearance of Raman signals indicate the loss of short-range order in NdCrO_3 ; and NdCrO_3 irradiated with 10^{15} Au-ions/ cm^2 shows featureless spectrum is noted as the most heavily damaged sample.

- **Au ions - NdAlO₃**

Raman spectra for the cross-sectioned NdAlO₃ sample irradiated with Au ions at fluence of 10¹⁵ Au ions/cm² are presented in **Figure 48**. Line mapping was performed from the surface to the depth of 19.5 μm with a step size of 1.5 μm. Raman spectra for NdAlO₃ sample (at the depth of 10.5 to 19.5 μm) are identical to the Raman spectra of pristine NdAlO₃ (Chapter 4, Figure 25) that show 8 Raman active modes. From the depth of 7.5 μm, these Raman bands show a slight broadening and all the Raman bands are clearly visible even at the depth of 3 μm. The most significant change occurs at the depth of 1.5 μm and no bands can be observed from the Raman spectra (**Figure 48**). Therefore, for this set of samples, some irradiation damage can be noted in the Raman spectra close to the sample surface, namely peaks intensity decrease and broadening of the peaks. From Raman spectra, it is found that the significant damage occurs at the depth of 1.5 μm, and this result is in agreement with SRIM calculation, which indicates the damage depth of 1.28 μm.

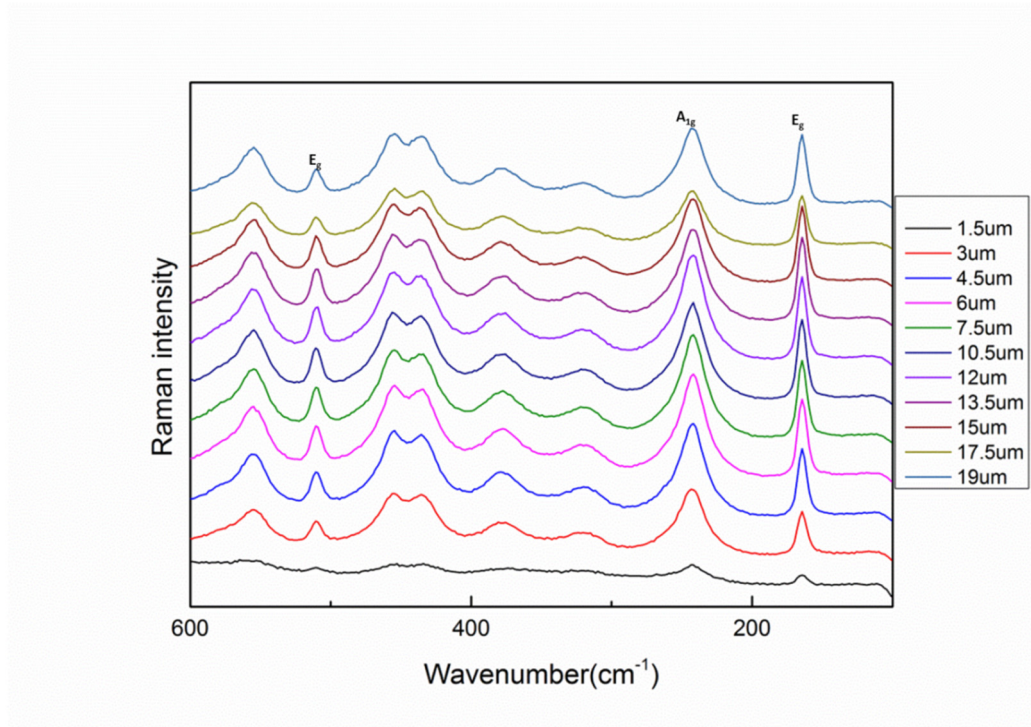


Figure 48. Raman spectra on cross-sectioned NdAlO₃ irradiated with 10^{15} Au-ions/cm².

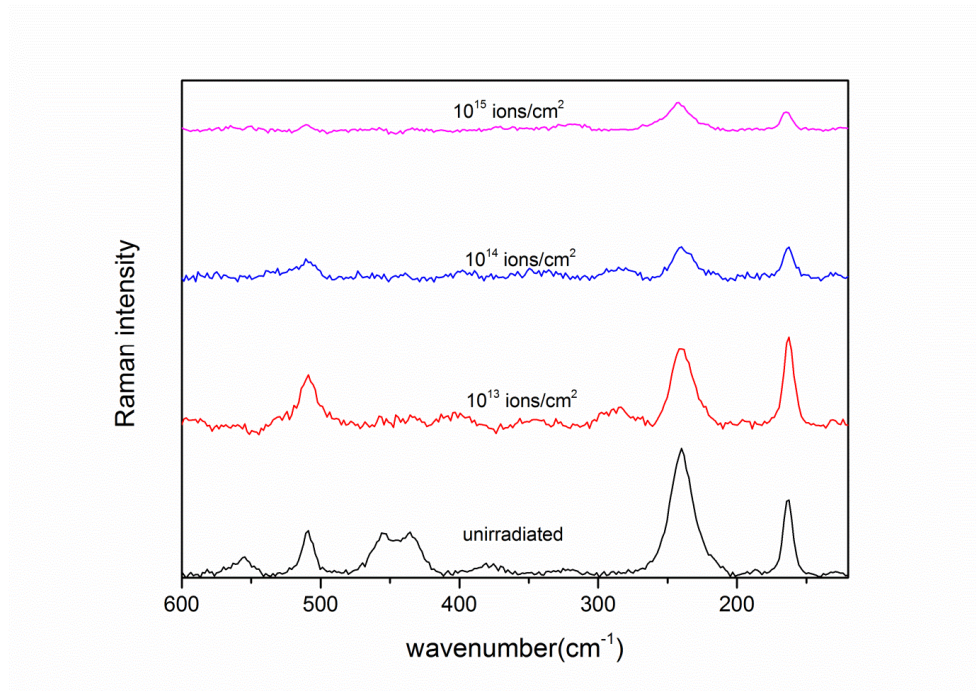


Figure 49. Raman microspectrometry spectra of sectioned pellets of pristine and Au-ion irradiated NdAlO₃.

Figure 49 presents the comparison of irradiated samples at various doses (10^{13} , 10^{14} , 10^{15} Au-ions/cm²) with pristine NdAlO₃. It can be observed that after being irradiated

with 10^{13} Au-ions/cm², peaks at the wavenumber of 163, 240 and 509 cm⁻¹ are still evident but show the loss of peaks intensity as well as the broadening of peaks; and these remaining bands are attributed to Nd³⁺ ions and AlO₆ octahedra [77]. However, peaks at wavenumber of 440, 454 and 556 cm⁻¹ disappeared, and these three Raman bands are assigned to the vibrations of Nd³⁺ in their own sites [78]. With increasing fluences, the remaining Raman peaks all show significant broadening and loss of peaks intensity; and there are only two very weak peaks at the wavenumber of 163 and 240 cm⁻¹ when NdAlO₃ followed 10^{15} Au-ions/cm² irradiation. The loss of peaks intensity, disappearance of Raman bands and broader bands that shown in Raman spectra indicate the loss of short-range order in irradiated NdAlO₃ and the effect increases with fluence. The observed band broadening and disappearance of Raman signals indicate significant radiation damage and the effect is most notable in the heavily damaged sample that received a dose of 10^{15} Au-ions/cm², which shows a featureless Raman spectrum with two very weak peaks at the wavenumber of about 163 and 240 cm⁻¹. Aside from these variations, it is observed that there is no peak shift between un-irradiated NdAlO₃ and sample followed 10^{14} Au-ions/cm², but there is band shift (2 cm⁻¹ wavenumber) towards higher wavenumber and this could be considered as experimental error.

Combining Raman results with GI-XRD results of NdCrO₃ and NdAlO₃ following Au ion irradiation, both show similar trend that 10^{13} Au-ions/cm² irradiation causes little damage with only slight loss of peak intensity in the XRD patterns, leaving approximately 90% crystallinity and only slight intensity loss and broadening of Raman bands with remaining Raman bands are still clearly visible. With increasing fluences, there is server loss of peak intensity in XRD patterns and eventually almost no peaks can be observed with the highest fluence (10^{15} Au-ions/cm²), which indicates the loss of long-range order and irradiation induced amorphization. As for Raman results, the most

heavily damage occurs at the fluence of 10^{15} Au-ions/cm² with only one to two very weak peaks exist indicate the loss of short-range order. These remaining peaks are related to CrO₆ or AlO₆ octahedra, respectively; and the presence of these weak peaks indicates some short-range order remains.

- **He ions- NdCrO₃**

Raman spectra measured at different depths for NdCrO₃ irradiated with 10^{17} He-ions/cm² are shown in **Figure 50**. Due to the uneven surface, 3 μm Raman scan was treated as surface. There is some evidence for band broadening in the spectra measured at depths of 3 to 12 μm where energy loss from electronic interactions is predominant [89, 90]. The effect is increasing and is particularly significant at the depth of 18 μm, and this corresponds to the end of the He-ion track where energy losses through nuclear displacements are maximized [90]. At depths of 19 to 45 μm, Raman spectra are similar to that of the pristine NdCrO₃ indicating that the implantation depth is below 19 μm and sample between the depths of 19 to 45 μm are undamaged. This damage depth concurs to the calculated depth using SRIM 2013 calculation (Chapter 3, Figure 19), which is 15.4 μm.

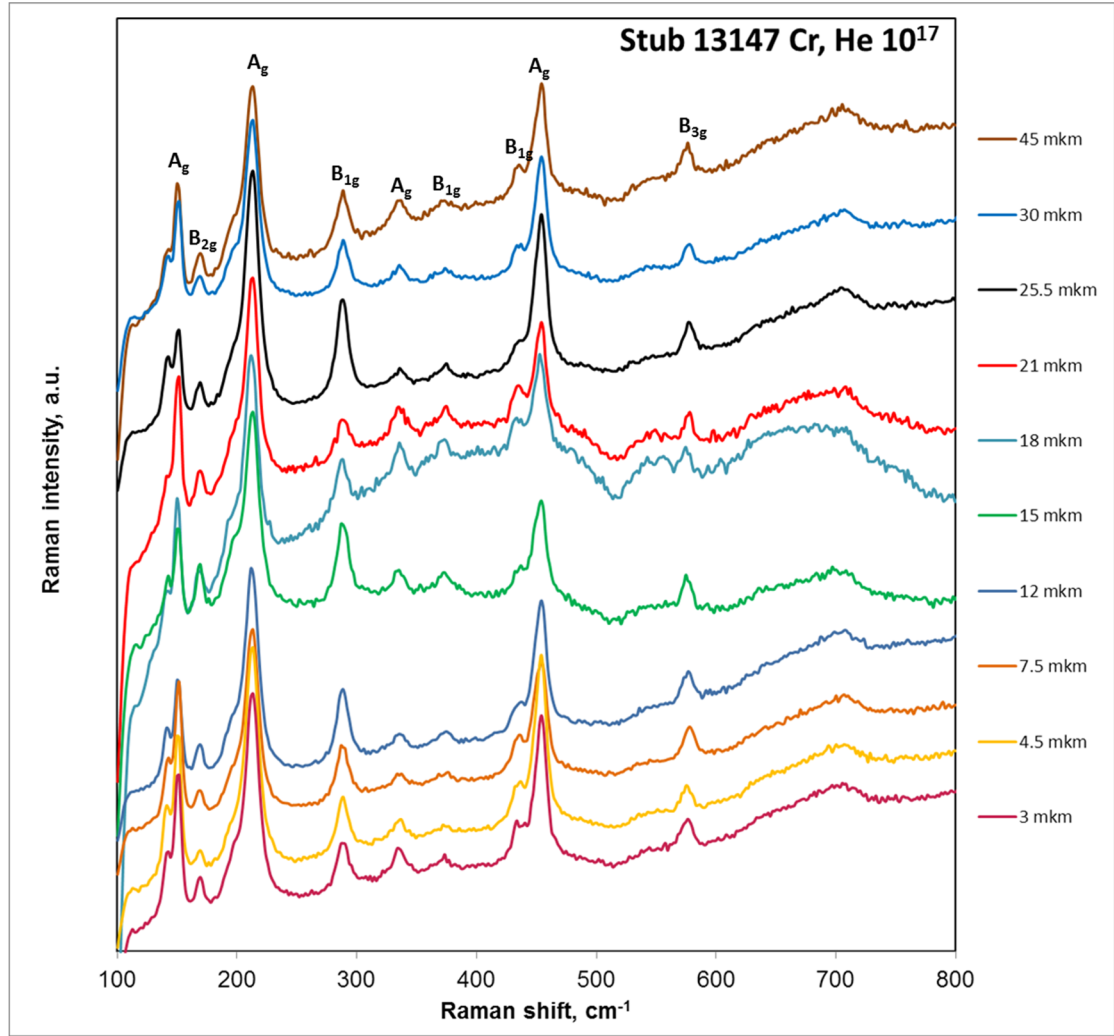


Figure 50. Raman spectra on NdCrO₃ following 10¹⁷ He-ions/cm² irradiation.

Figure 51 shows the Raman spectra of pristine NdCrO₃ and NdCrO₃ following 10¹⁷ He-ions/cm² irradiation at a constant depth of 18 μ m. The reason for choosing 18 μ m is that at the depth of 18 μ m, sample has been damaged most heavily, the deposited nuclear energy is significant and He ions transfer all its energy near the end of $\sim$ 18 μ m tracks [40, 90]. As NdCrO₃ is porous, it is not necessary to compare the intensity change between pristine and 10¹⁷ He-ions/cm² irradiated NdCrO₃. However, the bands broadening at the wavenumber of 240 and 700 cm⁻¹ with all the Raman bands still evident were observed and these Raman signals indicate there is little damage on NdCrO₃ irradiated with He ions up to 10¹⁷ ions/cm².

Actually, little difference between the Raman spectra of pristine and He ions irradiated NdCrO_3 is due to the kinetic energy deposition of He ions. The energy from 5 MeV He-ion irradiation is deposited into NdCrO_3 mainly through electronic interactions and a very small fraction of energy in the form of elastic collisions generating a few atomic displacements toward the end of the track which cause little damage on the sample [40, 90].

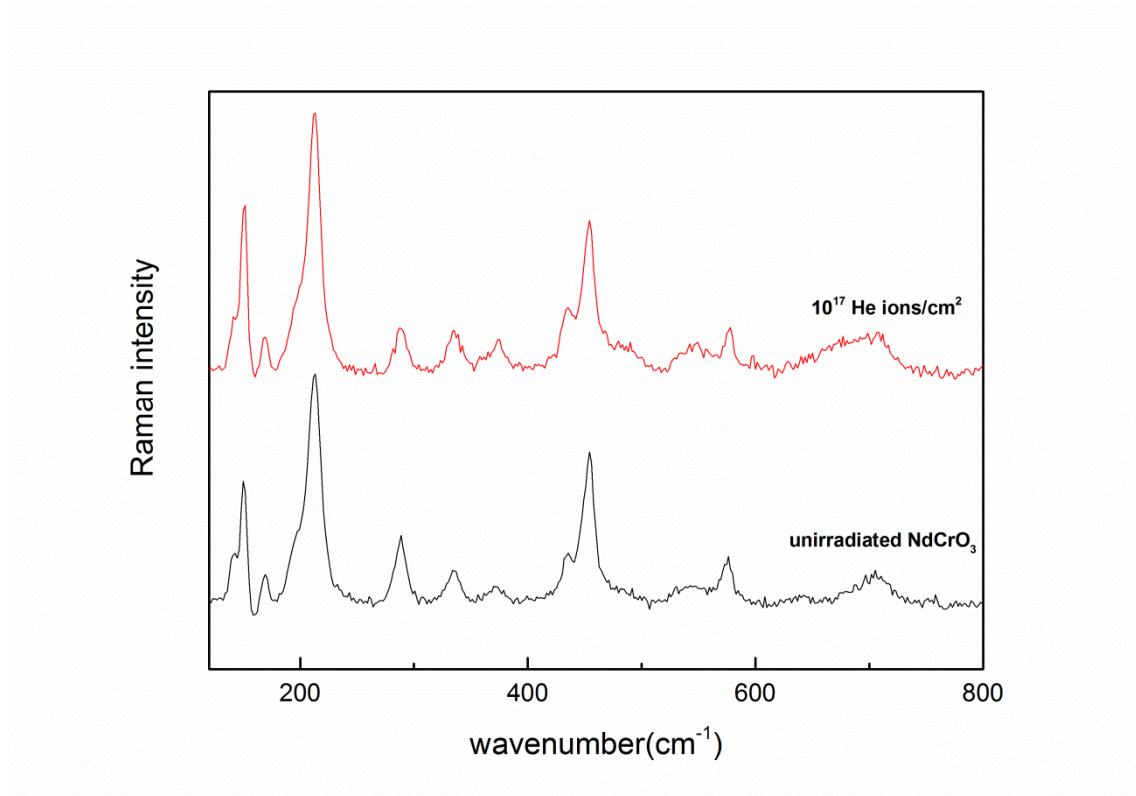


Figure 51. Raman microspectrometry spectra of sectioned pellets of pristine and 10^{17} He ions/ cm^2 irradiated NdCrO_3 taken at a depth of 18 μm .

- **He ions- NdAlO_3**

Figure 52 presents the Raman spectra of NdAlO_3 irradiated with 10^{17} He-ions/ cm^2 at different depth; 1.5 μm Raman scan is treated as surface, all Raman bands become broadened at the depth of 7.5 μm and the effect is particularly notable at the depth between 10.5 and 12 μm , where there is loss of peak intensity and peak broadening. At the depth of 12 μm and beyond, Raman spectra are similar to that of the pristine

NdAlO₃. This result corresponds to the SRIM calculation that the damage depth for NdAlO₃ irradiated with 10^{17} He-ions/cm² is 12.6 μ m.

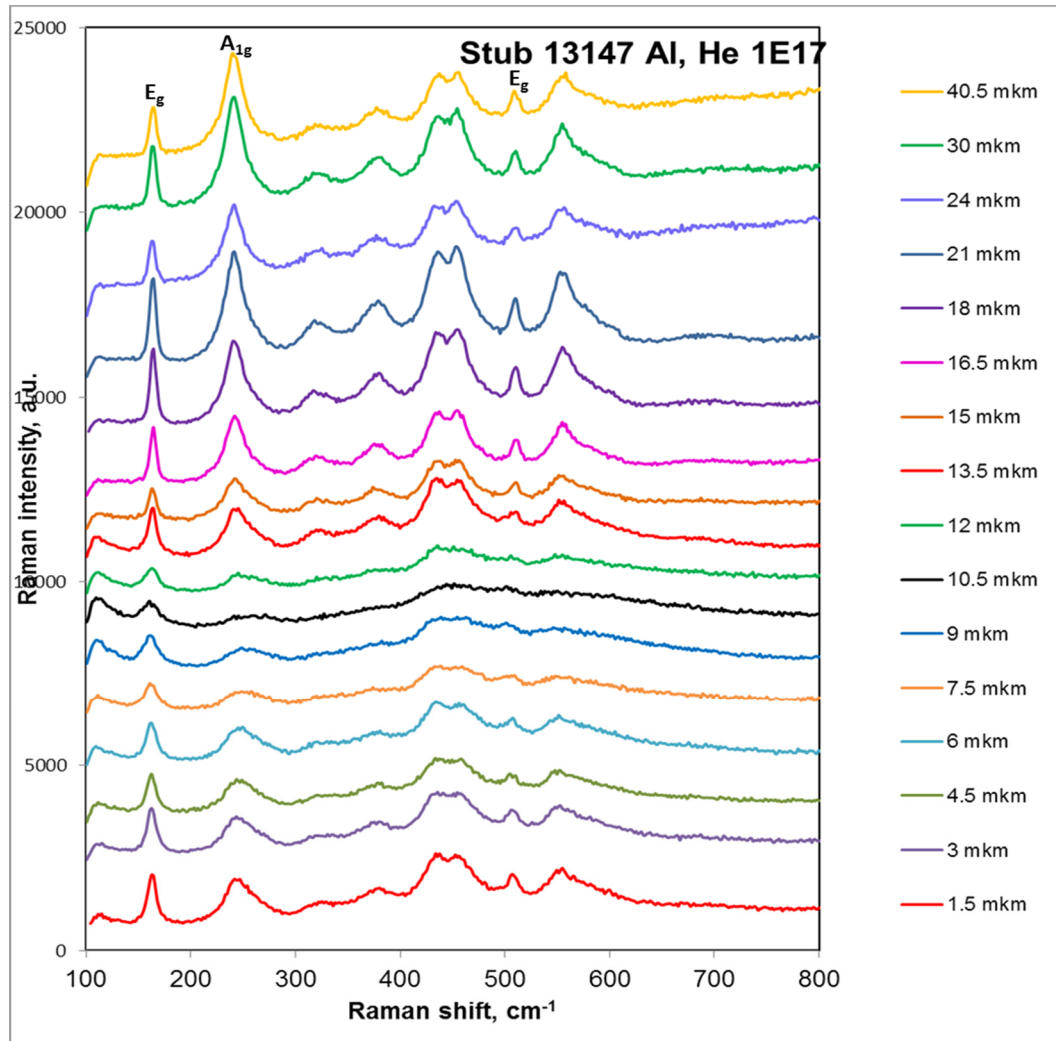


Figure 52. Raman spectra of NdAlO₃ following 10^{17} He-ions/cm² irradiation.

The following figure (**Figure 53**) shows the Raman spectra of sectioned pellets of pristine and He ion irradiated NdAlO₃ at a constant depth of 12 μ m and the reason for choosing this damage depth is the same as that for NdCrO₃ that mentioned above. The broadening of all bands can be observed with NdAlO₃ irradiated with 10^{16} He-ion/cm². The effect is more significant for NdAlO₃ following 10^{17} He-ions/cm² irradiation; all the Raman bands show severer band broadening, loss of peak intensity and the disappearance of peaks at the wavenumber of 510 and 560 cm⁻¹. He ions irradiation up

to 10^{17} ions/cm² do induce some damage on NdAlO₃ at the depth of 12 μ m and this corresponds to the end of the He-ion track where energy losses through nuclear displacement are maximized.

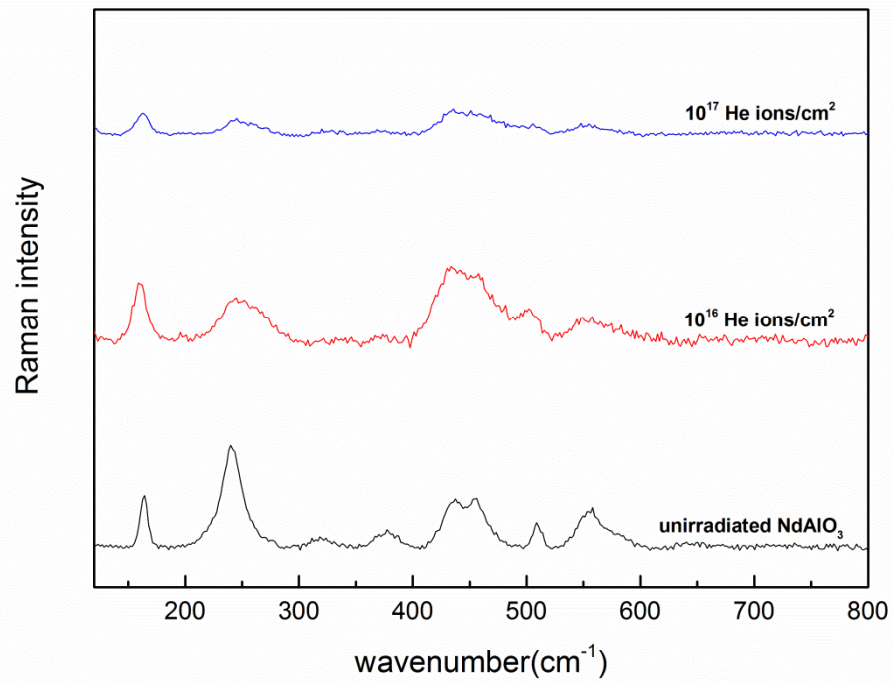


Figure 53. Raman microspectrometry spectra of sectioned pellets of pristine and He ion irradiated NdAlO₃. Spectra were taken at a depth of 12 μ m.

6.2.4 Hardness Measurements

The following figures show about 20 tests of the load on sample, and hardness as a function of displacement for un-irradiated NdAlO₃, NdCrO₃, and NdCrO₃ and NdAlO₃ irradiated with 10¹⁵ ions/cm² Au ions. The average hardness for each sample calculated using hardness from 200 to 400 nm displacement is presented in **Table 9**. **Table 10** presents the standard deviation of hardness (from 200 to 400 nm displacement) of un-irradiated and irradiated NdAlO₃ and NdCrO₃ to see the hardness fluctuation.

- NdAlO₃

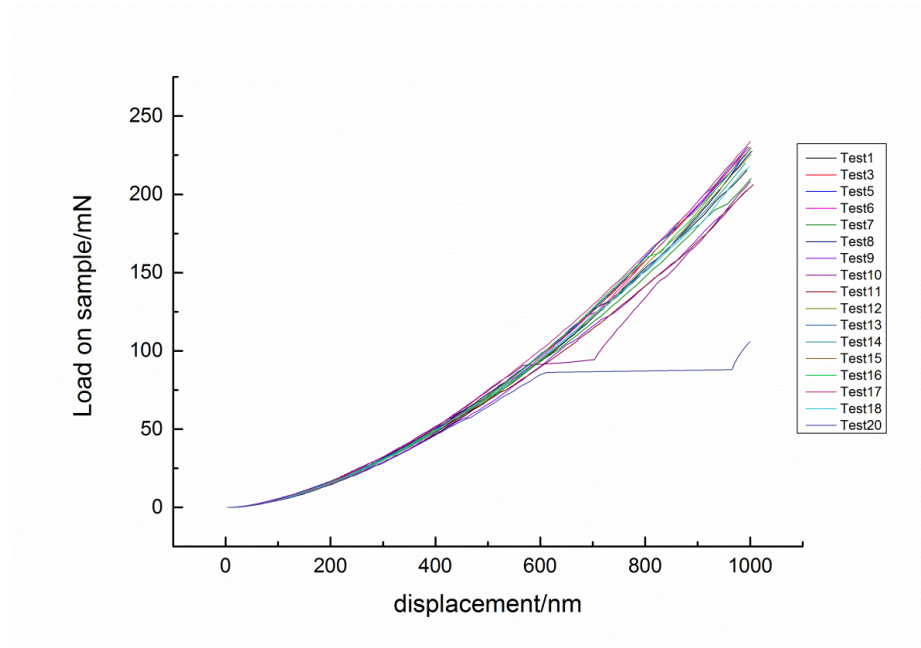


Figure 54. Load on sample versus displacement in un-irradiated NdAlO₃.

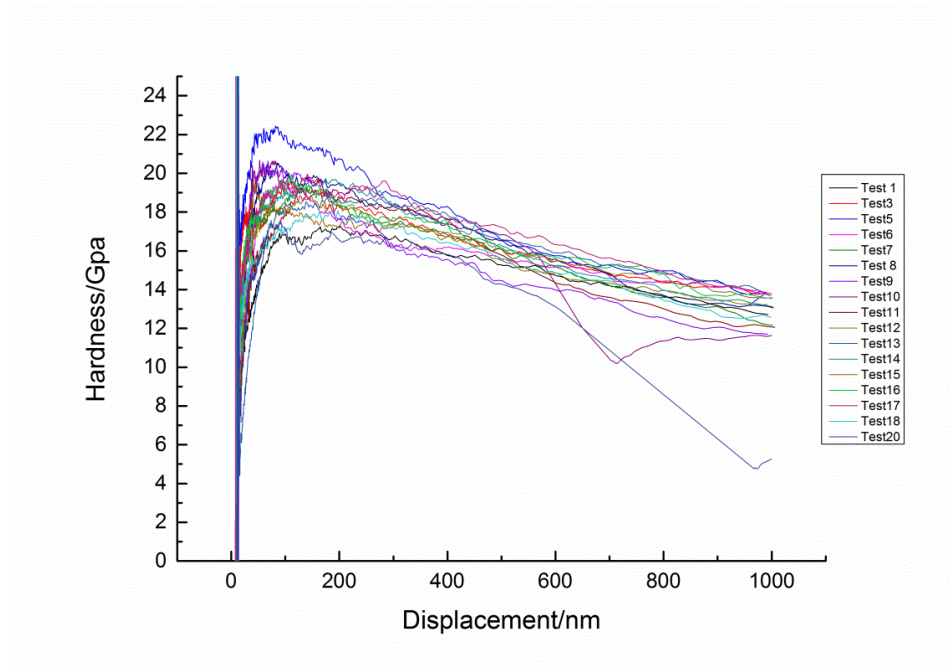


Figure 55. Hardness variation versus displacement in un-irradiated NdAlO₃.

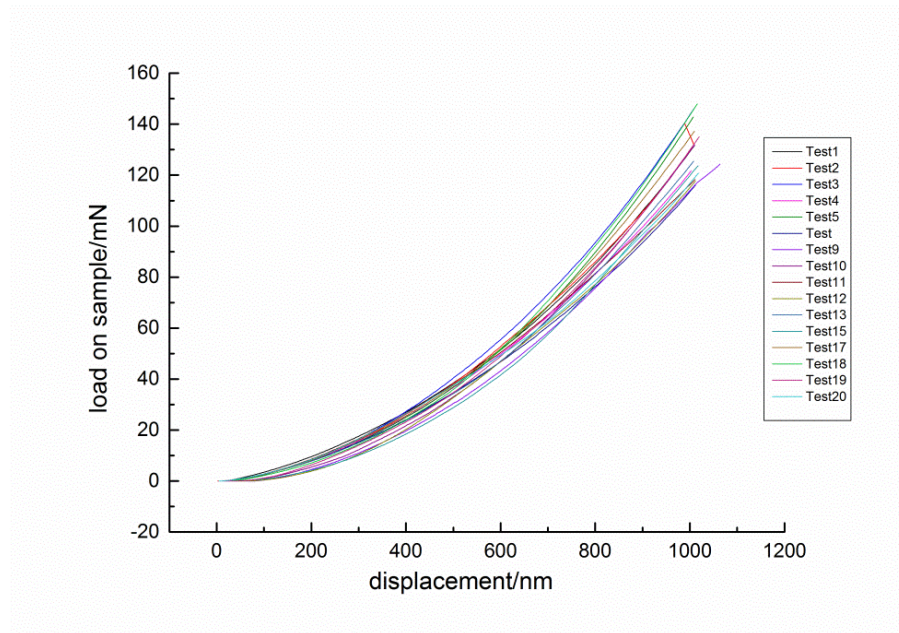


Figure 56. Load on sample versus displacement in NdAlO₃ irradiated with 10¹⁵ Au-ions/cm².

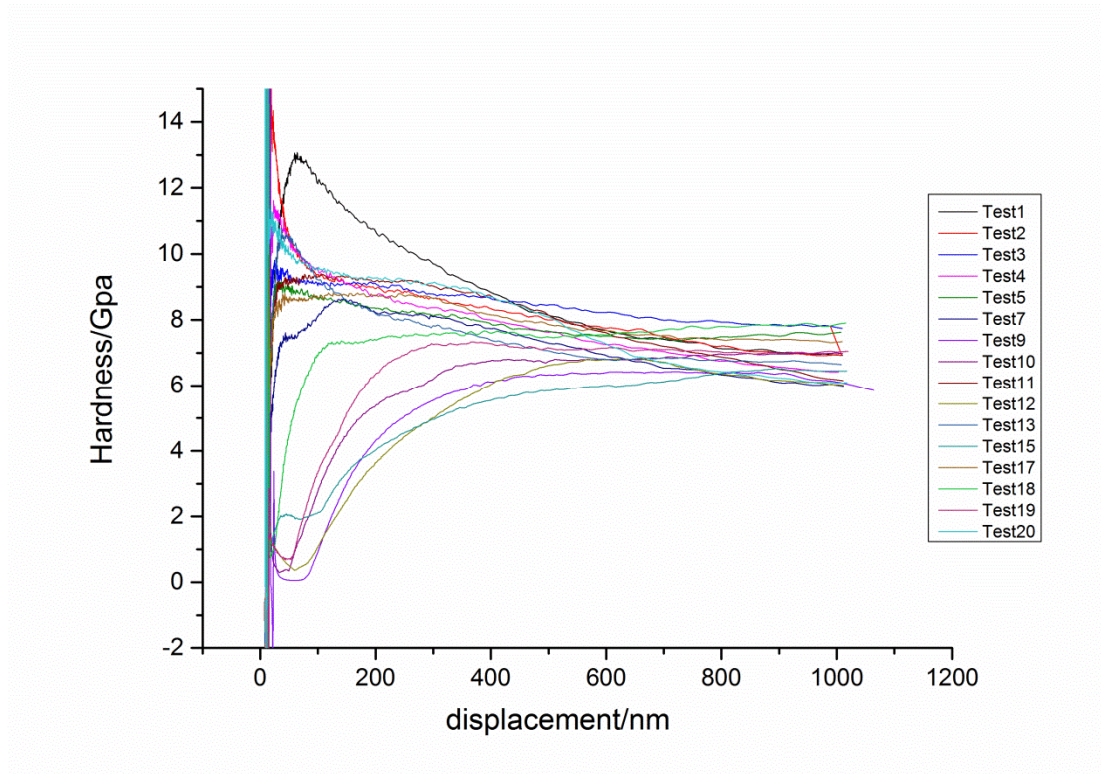


Figure 57. Hardness variation versus displacement in NdAlO₃ irradiated with 10¹⁵ Au-ions/cm².

- NdCrO₃

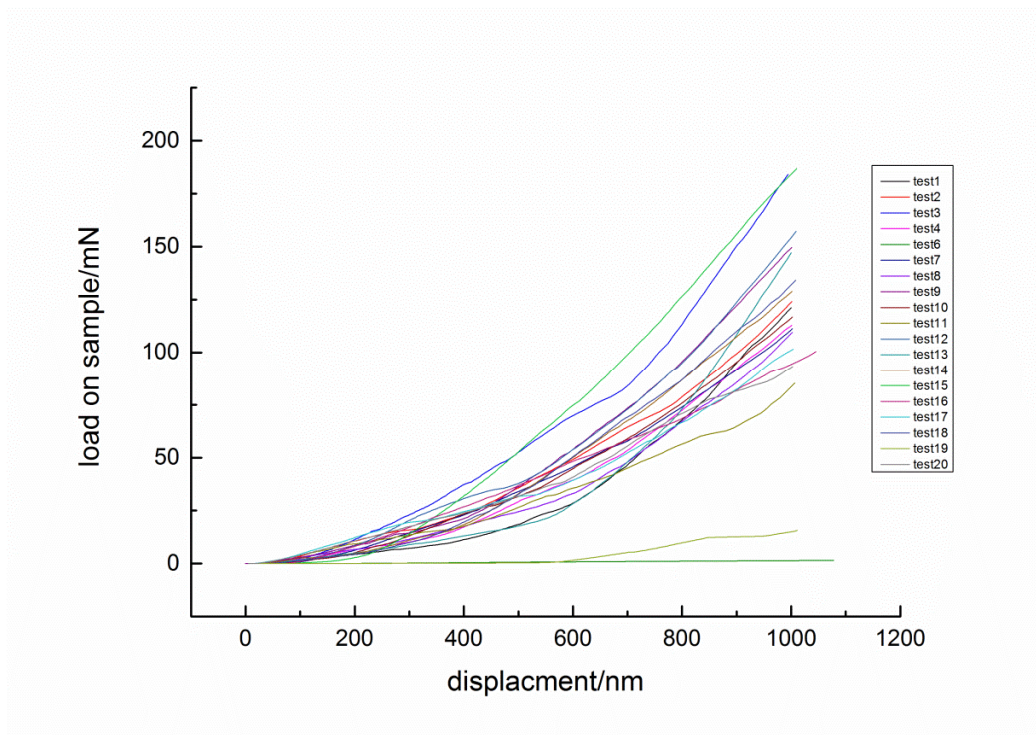


Figure 58. Load on sample versus displacement in un-irradiated NdCrO₃.

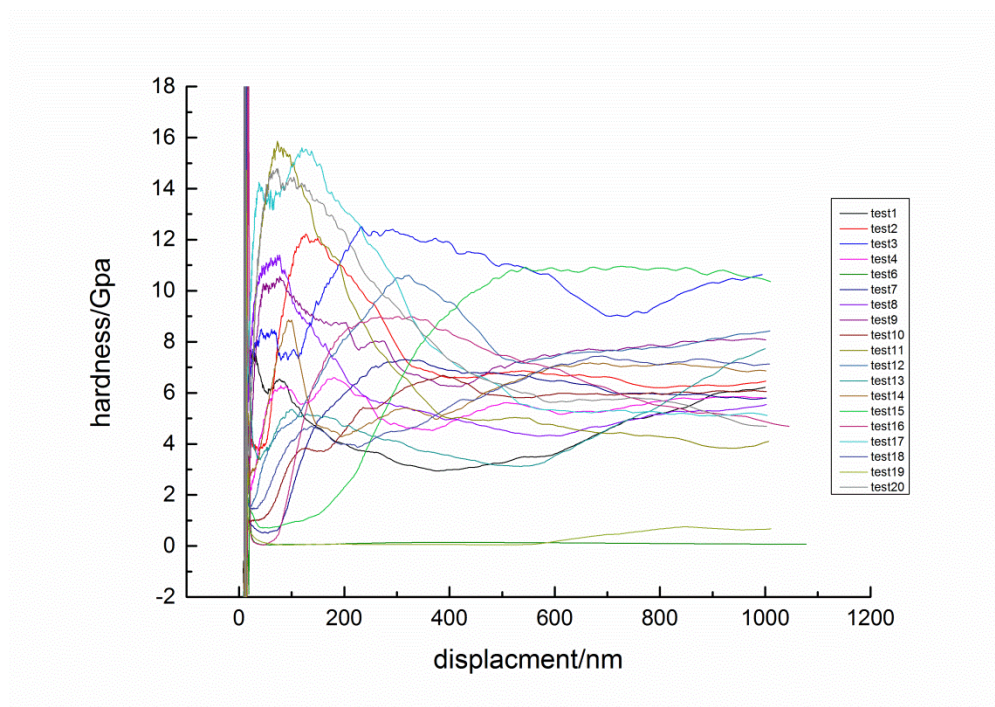


Figure 59. Hardness variation versus displacement in un-irradiated NdCrO₃.

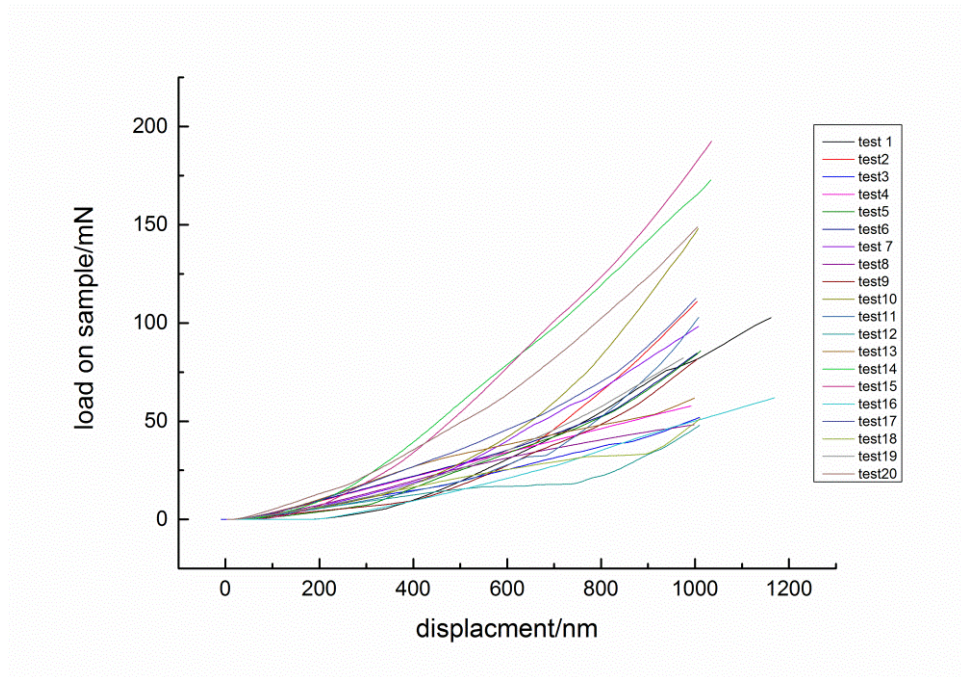


Figure 60. Load on sample versus displacement in NdCrO₃ irradiated with 10¹⁵ Au-ions/cm².

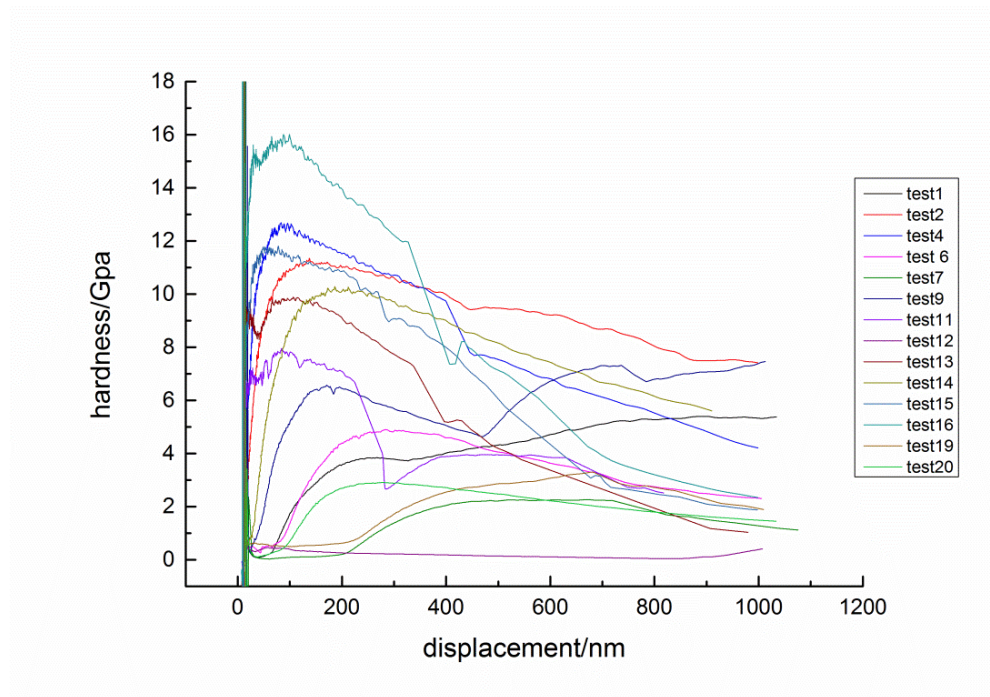


Figure 61. Hardness variation versus displacement in NdCrO₃ irradiated with 10¹⁵ Au-ions/cm².

Table 9. Average hardness of pristine and 10^{15} Au-ions/cm² irradiated NdCrO₃ and NdAlO₃.

Fluence Hardness(GPa)	Un-irradiated	10^{15} ions/cm ²
NdAlO ₃	18	8
NdCrO ₃	6	7

Table 10. Standard deviation of average hardness of pristine and 10^{15} Au-ions/cm² irradiated NdCrO₃ and NdAlO₃

Fluence Standard deviation	Un-irradiated	10^{15} ions/cm ²
NdAlO ₃	0.9	1.5
NdCrO ₃	3.2	3.1

From **Table 9**, compare with pristine NdAlO₃, as fluence increases, the hardness shows a downward trend. The hardness of NdAlO₃ decreases from 18 GPa to 8 GPa after irradiation and this hardness reduction is ~50% for material irradiated at 10^{15} ions/cm². The effects of α -decay induced amorphization on hardness have been studied previously in several ceramic phases and the phenomena of material softening after ion beam irradiation can be observed generally [34, 40, 90]. The literature from Weber et al. [34] explained that material softening with 10^{15} Au ions/cm² irradiation is due to irradiation induced amorphization that results in a lower density structure and eventually become softened. However, from SEM figures, it can be observed that NdAlO₃ irradiated with 10^{15} Au-ions/cm² seems to have the highest density, this can be explained that from GI-

XRD results of NdAlO_3 , it is found that with the increase of ion fluence, NdAlO_3 experienced significant radiation damage, and the sample eventually became near completely amorphous. From the hardness variation, it can be seen that the hardness of NdAlO_3 showed a decrease with increase of ion fluence. Combining with the results of GI-XRD and hardness variation, it is suggested that when NdAlO_3 was irradiated with 10^{15} Au-ions, it became near completely amorphous forming a glassy material with reduced hardness when compared to the initial crystalline state. The effects of α -decay induced amorphization on hardness have been studied previously in several ceramic phases and the phenomena of material softening after ion beam irradiation can be observed generally for ceramics.

In my case, the “densification” that can be observed from SEM figures is due to the amorphization and the formation of a glassy material with reduced porosity but the actual hardness reduces significantly during this process.

For variation of hardness of the NdCrO_3 samples, Au-ion irradiation appears to have little effect. For un-irradiated NdCrO_3 , the average hardness is 6 GPa, and after irradiation with 10^{15} Au-ions/cm², the hardness shows a slight increase to 7 GPa, although given the spread of the data, these results may be within the experimental error. As mentioned above, ceramic materials generally show softening after irradiation, while NdCrO_3 shows perhaps slight hardening. The possible explanation is through the porous nature of the material. As the material is amorphous, the pores in the damaged material may collapse, and this may densify the damaged material to some extent.

Standard deviation (**Table 10**) was calculated to show the spread of hardness data of each sample visually. For both un-irradiated and irradiated NdAlO_3 , the standard deviation is 0.9 and 1.5, respectively, which means that 20 tests of each sample have

similar trend and there is a little fluctuation between each test. This is in corresponding to **Figure 55** and **Figure 57**. However, the calculated standard deviation of NdCrO₃ and irradiated NdCrO₃ is more than 3, which indicates a larger spread of data between each test, and this is obvious in **Figure 59** and **Figure 61**. The calculated standard deviation further indicates that with the spread of data, we can only indicate general trends rather than accurate variations.

To sum up, it is better to measure the hardness of dense material, as the pores of material will have an impact on the measurement thus reducing accuracy. It is clear that NdCrO₃ and NdAlO₃ are not optimal materials for hardness measurements because of porosity, but it can still show general hardness trends. SEM figures have been summarized in Chapter 4 and they show that NdAlO₃ is a dense material with 1% porosity and therefore it shows the tendency of softening after irradiation similar to other ceramic materials. The porosity of NdCrO₃ that is shown clearly from the SEM figure (Chapter 4 Figure 23) is significant (23%) and this would have implications on hardness measurements before and after irradiation.

6.2.5 Thermal annealing after ion irradiation

GI-XRD was used to study the recrystallization and structural recovery of the ion-beam damaged samples following various heat treatments. In each case (NdCrO₃ and NdAlO₃), the most heavily damaged sample that received a fluence of 10¹⁵ Au-ions/cm², was annealed in air at temperatures between 600 and 1600°C in 2h. The XRD patterns of each sintering temperature are shown in **Figure 62** and **63** for NdCrO₃ and NdAlO₃, respectively.

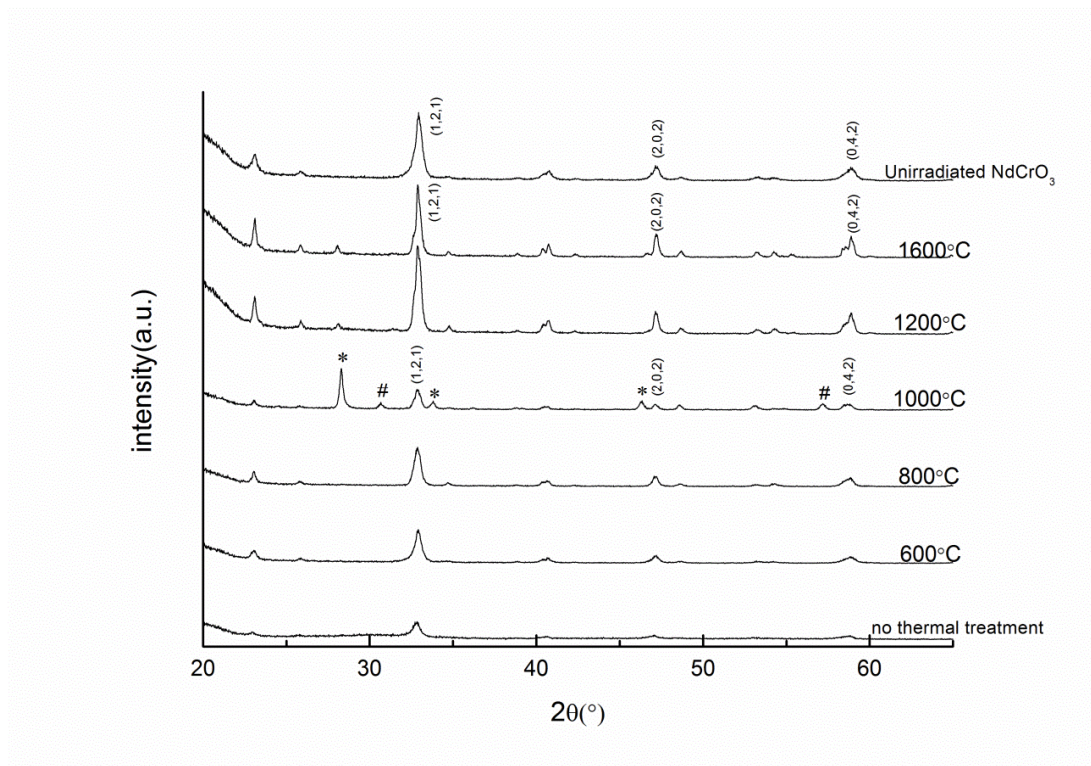


Figure 62. Temperature evolution of the GI-XRD data using a 2° incidence angle for NdCrO_3 with a fluence of 10^{15} Au-ions/ cm^2 . Samples are annealed for 2h at the designated temperature and then measured before further annealing at higher temperature. Patterns are plotted as diffraction intensity vs angle ($^\circ 2\theta$). Main peaks in the pattern are for NdCrO_3 , and # indicate neodymium oxide, * indicate chromium oxide.

For the Au-ion beam irradiated NdCrO_3 (**Figure 62**), significant increases in peak intensities are observed in the samples annealed at 600, 800 and 1200°C . The crystallinity of sample heated to 800°C is about 63.5% of that of the un-irradiated material. However, in the sample annealed at 1000°C , there are several extra peaks which appear around 28° , 30° , 46° and $56^\circ 2\theta$, which may indicate the presence of neodymium oxide (Nd_2O_3) and chromium oxide (CrO_3), respectively. The peaks around $28^\circ 2\theta$ are still evident at annealing temperature of 1200 and 1600°C , but the peaks are very weak. At these temperatures, most of the oxides have reacted to reform NdCrO_3 . After annealing NdCrO_3 to 1600°C , the crystallinity is almost identical when compared with the pristine material.

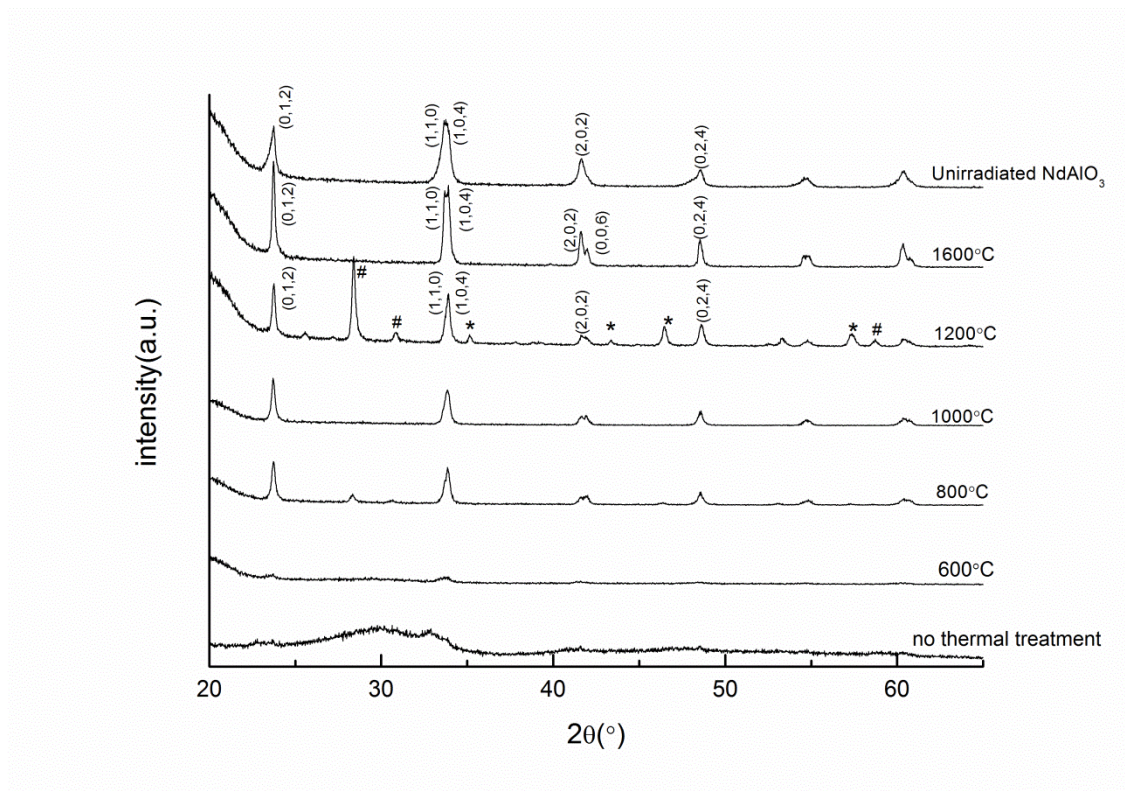


Figure 63. Temperature evolution of the GI-XRD data using a 2° incidence angle for NdAlO₃ with a fluence of 10¹⁵ Au-ions/cm². Samples are annealed for 2h at the designated temperature and then measured before further annealing at higher temperature. Patterns are plotted as diffraction intensity vs angle (°2θ). Main peaks in the pattern are for NdAlO₃, # indicate neodymium oxide and * indicate alumina.

For the Au-on beam irradiated NdAlO₃ (**Figure 63**), there were no significant variations in the XRD pattern could be seen following heat treatment at 600°C. However, the broad amorphous hump was no longer visible. Significant increases in peak intensities are observed in the samples annealed between 800 and 1200°C, the increase of intensity of the diffraction peaks corresponds to approximately a 55% recovery of the crystalline material annealed at 1000°C as compared with the undamaged sample. For the sample annealed at 1200°C, several extra peaks appear at around 28°, 30°, 45° and 54°, 57°, 58° 2θ. Aside from the peak around 28° 2θ which is an intense peak, all others are weak peaks. These peaks may indicate the presence of neodymium oxide (Nd₂O₃) and aluminium oxide (Al₂O₃) which are not reacted. Then, the sample was sintered to

1600°C, the XRD pattern exhibits the single rhombohedral structure with no extra peaks and the material is almost recovered to crystalline.

Overall, 5MeV He-ion irradiation was utilized on NdCrO₃ and NdAlO₃, and as a result of He-ion irradiation, it was not apparent in crystallographic contrast changes in the SEM; but the broadening in cross-sectional Raman spectroscopy indicated that significant damage had occurred at depths of around 15 μm, corresponding to the He-ion track. Au-ion irradiation was selected to simulate the recoil particle during α-decay processes. Au-ion irradiation resulted in an increase in samples volume, a loss in long-range order as determined by GI-XRD, NdAlO₃ material softening and NdCrO₃ material hardening. Raman spectroscopy implied notable distortion to the bonds in the CrO₆ and AlO₆ octahedra at high fluence. Crystallographic variations were observed through contrast changes in the SEM between 2 and 2.6 μm. Therefore, both materials appeared to become amorphous with macroscopic, mechanical and structure changes observed at fluences $\geq 10^{14}$ Au-ions/cm². These results above confirm that the properties of NdCrO₃ and NdAlO₃ have been modified due to nuclear effects.

In order to compare the radiation tolerance of Orthorhombic Pnma structure and Rhombohedral R-3c structure, it is necessary to compare the results from characterization of NdCrO₃ and NdAlO₃.

Specifically, at the fluence of 10^{13} Au-ions/cm², Raman spectra and GI-XRD results for both NdCrO₃ and NdAlO₃ materials show a few variations as almost all the XRD and Raman peaks still exist with only loss of peak intensity and slight peak shift; also, the crystallinity for both materials remain at about 90% of pristine materials. The effect is increasing with fluence for both materials, and at the dose of 10^{14} Au-ions/cm², NdAlO₃ experienced severer damage than NdCrO₃ as more dramatic loss of peak intensity together with peak shift were observed in NdAlO₃ GI-XRD patterns; and NdAlO₃ only

kept 18% crystallinity of pristine NdAlO₃ after irradiation, whereas NdCrO₃ remained about 56% crystallinity. NdAlO₃ became almost complete amorphous after irradiated with 10¹⁵ Au-ions/cm² as no peaks were observed in GI-XRD pattern as such no crystallinity could be calculated; While NdCrO₃, 15% crystallinity was observed. While for Raman spectra of both materials at the fluence higher than 10¹³ Au-ions/cm², both showed band broadening and became featureless at fluence of 10¹⁵ Au-ions/cm², which indicated the loss of short-range order in materials. As Raman spectroscopy is the complement of XRD analysis to study the effect of ion beam irradiation, therefore, combine GI-XRD with Raman results, it can be concluded that NdCrO₃ may have better radiation tolerance than that of NdAlO₃.

6.3 Conclusions

In this chapter, neodymium chromate and neodymium aluminate were irradiated with Au- and He-ions to simulate the effects of α -decay. Characterizations were utilized on neodymium chromate and neodymium aluminate following irradiation with Au ions at different doses (10¹³, 10¹⁴ and 10¹⁵ ions/cm²) and He ions at 10¹⁶ and 10¹⁷ ions/cm².

As for NdCrO₃ and NdAlO₃, 12MeV Au ions showed a significant volume swelling of ~7% and ~9%, a loss in long-range order at fluences above 10¹⁴ Au ions/cm², a slight increase in hardness of ~10% for NdCrO₃ and a reduction in hardness of ~50% for NdAlO₃. Raman analysis further demonstrated significant distortions of the CrO₆ and AlO₆ octahedra. Little effect on the materials effects was noted for NdCrO₃ and NdAlO₃ samples irradiated with 5MeV He ions up to a fluence of 10¹⁷ ions/cm², although broadening in the Raman spectra suggested some loss of short-range ordering at depths at the end of the He-ion track. Thermal treatment to the highest fluence Au-ion

irradiated NdCrO_3 and NdAlO_3 samples resulted in limited recovery of the crystalline structure at temperatures between 800 and 1200°C. At the higher temperature at 1600°C, NdCrO_3 and NdAlO_3 both showed nearly complete recovery of crystalline structure. NdCrO_3 showed perhaps better radiation tolerance than NdAlO_3 .

Chapter 7 Conclusion

In summary, nuclear power is popular to generate heat and due to the popularity of nuclear power, it is important to take the increase of nuclear fuel burn up as a consideration to make it much more economical. However, when additives such as Cr_2O_3 and Al_2O_3 added into the UO_2 fuel, PuCrO_3 and PuAlO_3 may be formed in this system and the presence of these Pu-doping phases may have impact on the properties of UO_2 and could have detrimental effects when stored as waste for a long time. Limited computational works focused on the behaviour of PuAlO_3 and PuCrO_3 indicated that the presence of PuCrO_3 and PuAlO_3 could cause alterations to the microstructure and macro-scale effects. In order to have a further understanding on PuCrO_3 and PuAlO_3 , we selected NdCrO_3 and NdAlO_3 as surrogates to simulate Pu-doping phases and the thermal conductivities and radiation tolerance of these two phases were investigated.

Firstly, NdCrO_3 and NdAlO_3 ceramics have been successfully synthesised using the co-precipitation method followed by conventional sintering. These two sintered samples were then characterized through X-ray diffraction (XRD), scanning electron microscopy (SEM) and Raman spectroscopy to identify their structure and purity. It was found that NdCrO_3 had the same structure (Orthorhombic Pnma) as PuCrO_3 , and NdAlO_3 possessed the same structure (Rhombohedral R-3c) as PuAlO_3 .

For the next step, thermal conductivities of these two materials were calculated by measuring the heat capacity, bulk density and thermal diffusivity. NdCrO_3 was found to have lower thermal conductivity than that of NdAlO_3 and it had lower thermal conductivity than that of UO_2 from literature. By contrast, NdAlO_3 held higher thermal

conductivity than both NdCrO₃ and UO₂, and this is similar when compared to values for the Pu-doped phases with UO₂ obtained through computational methods.

For the rest of these samples, neodymium chromate and neodymium aluminate were irradiated with Au- and He-ions to simulate the effects of α -decay. There were some characterizations utilized on samples following irradiation with Au ions at different fluences (10^{13} , 10^{14} and 10^{15} ions/cm²) and He ions at 10^{16} and 10^{17} ions/cm². For NdCrO₃ and NdAlO₃, 12MeV Au ions showed a significant volume swelling of ~7% and ~9%, a loss in long-range order at fluences above 10^{14} Au ions/cm², a slight increase in hardness of ~10% for NdCrO₃ and a reduction in hardness of ~50% for NdAlO₃. Raman analysis further demonstrated significant distortions of the CrO₆ and AlO₆ octahedra. By contrast, there was little effect on the materials effects was observed for NdCrO₃ and NdAlO₃ samples irradiated with 5MeV He ions up to a fluence of 10^{17} ions/cm², although some loss of short-range order could be observed through broadening in the Raman spectra at depths at the end of the He-ion track. Thermal treatment to the highest fluence Au-ion irradiated NdCrO₃ and NdAlO₃ samples resulted in limited recovery of the crystalline structure at temperatures between 800 and 1200°C. At the higher temperature at 1600°C, NdCrO₃ and NdAlO₃ both showed nearly complete recovery of crystalline structure.

Overall, NdCrO₃ had lower thermal conductivity than that of NdAlO₃ and UO₂, while showed perhaps better radiation tolerance than NdAlO₃. As neodymium was selected as the surrogate of plutonium, therefore, it could be concluded that the presence of these Pu-doping phases (PuCrO₃ and PuAlO₃) may have significant effect on the thermal behaviour and properties of the UO₂.

As for this project, it has some contributions:

- It provided a detailed description of the synthesis of neodymium chromate and neodymium aluminate; gave guidance on how to measure the thermal conductivity and characterize on samples following ion beam irradiation.
- It measured the thermal conductivity of NdCrO_3 and NdAlO_3 at high temperature that above 1000°C and this is helpful to simulate the variation of thermal conductivity of Pu-doping phases at elevated temperatures.

From this project, one will be able to have comprehensive knowledge about the synthesis procedure, the thermal conductivity and radiation tolerance of NdCrO_3 and NdAlO_3 . With this understanding, it will be helpful for the further investigation on PuCrO_3 and PuAlO_3 or other phases that could be formed in nuclear materials.

Within this project, there is still a long way to understand how these Pu-doping phases can affect the thermal behaviour and properties of UO_2 ; as NdAlO_3 and NdCrO_3 are only selected as surrogates and are for simulation only. In order to get accurate result of thermal conductivity and radiation tolerance of NdCrO_3 and NdAlO_3 and make better prediction, some future works are recommended here:

- Perspective on our experiment itself, when synthesize NdCrO_3 pellets, it was found that it is difficult to synthesize dense NdCrO_3 sample and the grain size is very fine that may be an obstacle for ion beam irradiation. Therefore, it is necessary to decrease the porosity and increase the grain size of NdCrO_3 . This may be done by increasing the sintering temperature or time such that the grain size can compact better or by using alternative techniques such as hot isostatic pressing or spark plasma pressing.
- For the investigation on the hardness of NdCrO_3 , because of the porosity of NdCrO_3 , the measured variation of hardness was different from the general trend

of other ceramics. By increasing the density and decreasing the porosity of NdCrO_3 , the hardness could be measured more accurately and other characterization techniques may also be employed.

References

1. Agency, I.E., *Key World Energy Statistics* <https://www.iea.org/publications/freepublications/>. 2012.
2. Nrel.gov., "Collectively, life cycle assessment literature shows that nuclear power is similar to other renewable and much lower than fossil fuel in total life cycle GHG emissions." http://www.nrel.gov/analysis/sustain_lca_nuclear.html. 2013.
3. Michael, I.O. and W. Lee, *An introduction to nuclear waste immobilisation*. 2005, Elsevier, Amsterdam.
4. *Radioactive waste* https://en.wikipedia.org/wiki/Radioactive_waste.
5. Afanasyev, A. and G. Raspopin, *Fuel cycle economical improvement by reaching high fuel burnup*. Technical and economic limits to fuel burnup extension, 2002: p. 304.
6. Fullarton, M.L., et al., *Structure, properties and formation of PuCrO₃ and PuAlO₃ of relevance to doped nuclear fuels*. Journal of Materials Chemistry A, 2013. 1(46): p. 14633-14640.
7. Russell, L., J. Harrison, and N. Brett, *Perovskite-type compounds based on plutonium*. Journal of Nuclear Materials, 1960. 2(4): p. 310-320.
8. Shannon, R.t., *Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides*. Acta Crystallographica Section A: Crystal Physics, Diffraction, Theoretical and General Crystallography, 1976. 32(5): p. 751-767.
9. Konings, R., *Comprehensive Nuclear Materials: Online Version*. Vol. 5. 2011: Newnes.
10. Cahill, D.G. and R. Pohl, *Lattice vibrations and heat transport in crystals and glasses*. Annual Review of Physical Chemistry, 1988. 39(1): p. 93-121.
11. Slack, G.A., *The thermal conductivity of nonmetallic crystals*. Solid state physics, 1979. 34: p. 1-71.
12. Drabble, J.T.G., H.J., *Thermal Conduction in Semi-conductors*. 1962.
13. Jones, W. and N.H. March, *Theoretical solid state physics: Perfect lattices in equilibrium*. Vol. 1. 1985: Courier Dover Publications.
14. Debye, P.J.W., et al., *Vorträge über die kinetische Theorie der Materie und der Elektrizität*. Vol. 6. 1914: BG Teubner.
15. Peierls, R.E., *Annln Phys*. 1929. 3: p. 1055.
16. Klemens, P. and M. Gell, *Thermal conductivity of thermal barrier coatings*. Materials Science and Engineering: A, 1998. 245(2): p. 143-149.
17. Vineis, C.J., et al., *Nanostructured thermoelectrics: big efficiency gains from small features*. Advanced Materials, 2010. 22(36): p. 3970-3980.
18. Bux, S.K., J.-P. Fleurial, and R.B. Kaner, *Nanostructured materials for thermoelectric applications*. Chemical Communications, 2010. 46(44): p. 8311-8324.
19. Minnich, A., et al., *Bulk nanostructured thermoelectric materials: current research and future prospects*. Energy & Environmental Science, 2009. 2(5): p. 466-479.
20. Meisner, G., et al., *Structure and lattice thermal conductivity of fractionally filled skutterudites: Solid solutions of fully filled and unfilled end members*. Physical review letters, 1998. 80(16): p. 3551.

21. http://en.wikipedia.org/wiki/Debye_model.
22. C.Kittel, *Introduction to Solid State Physics*. 1986.
23. Debye model https://en.wikipedia.org/wiki/Debye_model#cite_note-2
24. *thermal conductivity*
https://en.wikipedia.org/wiki/Thermal_conductivity#cite_note-6.
25. Castro, M.L.V.R.C.A.N.d., *Standard Reference Data for the Thermal Conductivity of Water*
26. *Sapphire, Al₂O₃*. <http://www.almazoptics.com/sapphire.htm>.
27. Association, W.N., *Synroc Wasteform* <http://www.world-nuclear.org/info/Nuclear-Fuel-Cycle/Nuclear-Wastes/Synroc/>.
28. Jostsons, A., *Synroc-progress and future prospects*. 2001.
29. *How does Synroc work?* <https://www.youtube.com/watch?v=krN2UEbaaxQ>.
30. *Synroc waste form*
<http://www.ansto.gov.au/cs/groups/corporate/documents/document/mdaw/mdi5/~edisp/acs056751.pdf>.
31. Norgett, M., M. Robinson, and I. Torrens, *A proposed method of calculating displacement dose rates*. *Nuclear Engineering and Design*, 1975. 33(1): p. 50-54.
32. Agency, N.E., *Primary Radiation Damage in Materials*.
33. Linn, B., *Radiation Damage Effects in Materials: Damage Formation Models*. 2013.
34. Weber, W.J., et al., *Radiation effects in crystalline ceramics for the immobilization of high-level nuclear waste and plutonium*. *Journal of Materials Research*, 1998. 13(06): p. 1434-1484.
35. Matsunaga, A., et al., *Radiation-induced amorphization and swelling in ceramics*. *Journal of nuclear materials*, 1991. 179: p. 457-460.
36. Wang, S., L. Wang, and R. Ewing, *Irradiation-induced amorphization: Effects of temperature, ion mass, cascade size, and dose rate*. *Physical Review B*, 2000. 63(2): p. 024105.
37. Hobbs, L.W., et al., *Radiation effects in ceramics*. *Journal of Nuclear Materials*, 1994. 216: p. 291-321.
38. Naguib, H. and R. Kelly, *Criteria for bombardment-induced structural changes in non-metallic solids*. *Radiation effects*, 1975. 25(1): p. 1-12.
39. R.S.Wilks, *J.Nucl.Mater*, 1968. 26: p. 13.
40. Picot, V., et al., *Ion beam radiation effects in monazite*. *Journal of Nuclear Materials*, 2008. 381(3): p. 290-296.
41. Mazey, D., *Fundamental aspects of high-energy ion-beam simulation techniques and their relevance to fusion materials studies*. *Journal of nuclear materials*, 1990. 174(2): p. 196-209.
42. Ziegler, J., J. Biersack, and U. Littmark, *The Stopping and Range of Ions in Matter* Pergamon Press. New York, 1985.
43. *Perovskite* <http://webmineral.com/data/Perovskite.shtml#VklJaiSzmc>.
44. Navrotsky, A., *Energetics and crystal chemical systematics among ilmenite, lithium niobate, and perovskite structures*. *Chemistry of materials*, 1998. 10(10): p. 2787-2793.
45. Levy, M.R., *Crystal structure and defect property predictions in ceramic materials*. 2005, University of London.
46. Harilal, M., et al., *Electrical and optical properties of NdAlO₃ synthesized by an optimized combustion process*. *Materials Characterization*, 2014. 90: p. 7-12.

47. Taguchi, H., M. Nagao, and Y. Takeda, *Relationship between the Electrical Properties and Crystal Structure of $(La_{1-x}Nd_x)CrO_3$ ($0 \leq x \leq 1.0$)*. Journal of Solid State Chemistry, 1995. 114(1): p. 236-241.
48. Riedel, R. and I.-W. Chen, *Ceramics Science and Technology, Materials and Properties*. Vol. 2. 2011: John Wiley & Sons.
49. Nakamura, T., G. Petzow, and L. Gauckler, *Stability of the perovskite phase $LaBO_3$ ($B = V, Cr, Mn, Fe, Co, Ni$) in reducing atmosphere I. Experimental results*. Materials Research Bulletin, 1979. 14(5): p. 649-659.
50. Badwal, S., *Stability of solid oxide fuel cell components*. Solid State Ionics, 2001. 143(1): p. 39-46.
51. Ring, T.A., *Fundamentals of ceramic powder processing and synthesis*. 1996: Academic Press. 81-83.
52. Munir, Z., U. Anselmi-Tamburini, and M. Ohyanagi, *The effect of electric field and pressure on the synthesis and consolidation of materials: a review of the spark plasma sintering method*. Journal of Materials Science, 2006. 41(3): p. 763-777.
53. Battison, J.M., *Cold Isostatic Pressing (CIP)*
http://www.mpif.org/ncrf/11/100813_cold_isostatic_pressing.pdf.
54. Lutique, S., et al., *The thermal conductivity of $Nd_2Zr_2O_7$ pyrochlore and the thermal behaviour of pyrochlore-based inert matrix fuel*. Journal of alloys and compounds, 2003. 352(1): p. 1-5.
55. Bragg, W. and W. Bragg, *The reflection of X-rays by crystals*. Proceedings of the Royal Society of London. Series A, Containing Papers of a Mathematical and Physical Character, 1913: p. 428-438.
56. Huang, T. and P. Predecki, *Grazing-Incidence X-Ray Technique For Surface, Interface, And Thin-Film Analysis*. 1997, JCPDS-International Center for Diffraction Data.
57. Goldstein, J.I., et al., *Preparation of biological samples for scanning electron microscopy*, in *Scanning Electron Microscopy and X-Ray Microanalysis*. 1981, Springer. p. 495-539.
58. Jaksch, H. *Strain related Contrast mechanisms in crystalline materials imaged with AsB detection*. in *EMC 2008 14th European Microscopy Congress 1–5 September 2008, Aachen, Germany*. 2008. Springer.
59. Harris, D. and M. Bertolucci, *Symmetry and Spectroscopy: an introduction to vibrational and electronic spectroscopy*. 1989. Mineola, NY: Dover Publications.
60. Hunn, J., et al., *Helium and hydrogen induced hardening in 316LN stainless steel*. Journal of nuclear materials, 2000. 282(2): p. 131-136.
61. Hunn, J., et al., *Ion-irradiation-induced hardening in Inconel 718*. Journal of nuclear materials, 2001. 296(1): p. 203-209.
62. Kerbiriou, X., et al., *Amorphization and dynamic annealing of hexagonal SiC upon heavy-ion irradiation: Effects on swelling and mechanical properties*. Journal of Applied Physics, 2009. 105(7): p. 073513.
63. Agilent Technologies, <http://cp.literature.agilent.com/litweb/pdf/5990-4178EN.pdf>.
64. MTS Test works,
http://www.mts.com/ucm/groups/public/documents/library/dev_002046.pdf.
65. Miura, T., et al., *Influence of crystal orientation on hardness and nanoindentation deformation in ion-irradiated stainless steels*. Journal of Nuclear Materials, 2011. 417(1): p. 984-987.
66. *Annealing (metallurgy)* [https://en.wikipedia.org/wiki/Annealing_\(metallurgy\)](https://en.wikipedia.org/wiki/Annealing_(metallurgy)).

67. Verhoeven, J.D., *Fundamentals of physical metallurgy*. 1975: Wiley New York.
68. Biersack, J. and J. Ziegler, *The Stopping and Ranges of Ions in Matter*, vol. 1 Pergamon. New York, 1985.
69. ANTARES Accelerator
<http://www.ansto.gov.au/ResearchHub/IER/Facilities/ANTARES/>.
70. Runnalls, O. *PHASE EQUILIBRIA STUDIES ON THE ALUMINIUM--PLUTONIUM SYSTEM*. in pp 341-57 of *Plutonium 1965. Proceedings of the Third International Conference on Plutonium, London, November 22--26, 1965*. Kay, AE Waldron, MB (eds.). New York, Barnes and Noble, Inc., 1. 1967. Chalk River Nuclear Labs., Ont.
71. L. E. Russell, D.L.H.a.N.H.B., *Journal of nuclear materials*, 1960. 2: p. 310.
72. Runka, T. and M. Berkowski, *Perovskite $\text{La}_{1-x}\text{Sr}_x\text{Ga}_{1-y}\text{Mn}_y\text{O}_3$ solid solution crystals: Raman spectroscopy characterization*. *Journal of Materials Science*, 2012. 47(14): p. 5393-5401.
73. Du, Y., et al., *Structure, magnetic, and thermal properties of $\text{Nd}_{1-x}\text{La}_x\text{CrO}_3$ ($0 \leq x \leq 1.0$)*. *Journal of Applied Physics*, 2010. 108(9): p. 093914.
74. Bhadram, V.S., et al., *Effect of pressure on octahedral distortions in RCrO_3 ($R = \text{Lu, Tb, Gd, Eu, Sm}$): the role of R-ion size and its implications*. *Materials Research Express*, 2014. 1(2): p. 026111.
75. Wang, S., et al., *Low temperature hydrothermal synthesis, structure and magnetic properties of RECrO_3 ($\text{RE} = \text{La, Pr, Nd, Sm}$)*. *Dalton Transactions*, 2015.
76. Zhao, J., et al., *High-pressure crystallography of rhombohedral PrAlO_3 perovskite*. *Journal of Physics: Condensed Matter*, 2009. 21(23): p. 235403.
77. Iliev, M., et al., *Raman spectroscopy of orthorhombic perovskitelike YMnO_3 and LaMnO_3* . *Physical Review B*, 1998. 57(5): p. 2872.
78. Marcondes, S., et al., *Resonance Raman spectroscopy of NdAlO_3 single-crystal fibers grown by the laser-heated pedestal growth technique*. *Vibrational Spectroscopy*, 2014. 73: p. 144-149.
79. Krishnan, R.V., et al., *Heat capacity and thermal expansion of uranium-gadolinium mixed oxides*. *Journal of Nuclear and Radiochemical Sciences*, 2009. 10(1): p. 1_19-1_26.
80. Kang, K.H., et al., *Thermal expansion of UO_2 and simulated DUPIC fuel*. *Journal of nuclear materials*, 2002. 301(2): p. 242-244.
81. Hirai, M., *Thermal diffusivity of $\text{UO}_2\text{-Gd}_2\text{O}_3$ pellets*. *Journal of nuclear materials*, 1990. 173(3): p. 247-254.
82. Pillai, C. and A. George, *Thermal conductivity of uranium dioxide*. *Journal of nuclear materials*, 1993. 200(1): p. 78-81.
83. Fink, J., *Thermophysical properties of uranium dioxide*. *Journal of nuclear materials*, 2000. 279(1): p. 1-18.
84. Arborelius, J., et al., *Advanced doped UO_2 pellets in LWR applications*. *Journal of nuclear science and technology*, 2006. 43(9): p. 967-976.
85. Wang, S.-X., et al., *Radiation stability of gadolinium zirconate: a waste form for plutonium disposition*. *Journal of Materials Research*, 1999. 14(12): p. 4470-4473.
86. M Mizuno, T.Y., T Noguchi, Yogyo Kyokaishi, 1977. 85: p. 52.
87. Nasdala, L., G. Irmer, and D. Wolf, *The degree of metamictization in zircons: a Raman spectroscopic study*. *European Journal of Mineralogy-Ohne Beihefte*, 1995. 7(3): p. 471-478.

88. Seydoux-Guillaume, A.-M., et al., *An XRD, TEM and Raman study of experimentally annealed natural monazite*. Physics and Chemistry of Minerals, 2002. 29(4): p. 240-253.
89. Zhang, S.-M., et al., *Influences on proton exchange by He ion implantation in LiNbO₃*. Optical Materials Express, 2015. 5(7): p. 1526-1531.
90. Gregg, D.J., et al., *Ion beam irradiation effects in strontium zirconium phosphate with NZP-structure type*. Journal of Nuclear Materials, 2014. 446(1): p. 224-231.