

High Voltage Electron Microscopy Study on Microstructure Evolution in Yttria-stabilized Cubic Zirconia

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High Voltage Electron Microscopy Study on Microstructure Evolution in Yttria-stabilized Cubic Zirconia

A dissertation submitted to the department of
Applied Quantum Physics and Nuclear Engineering
in partial fulfillment of the requirements
for the degree of

DOCTOR OF ENGINEERING

By

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*To **Sampa** and **Luban**- for their support and caring*

&

*To my **parents**- for their love and blessings*

Abstract

Yttria-stabilized cubic zirconia (YSZ) with a fluorite-type structure has attracted enormous attention due to its exceptional radiation tolerant quality against extreme radiation environment, and it is, therefore, considered to be matrices of nuclear reactor fuel and transmutation target for actinides. In these applications, YSZ should subsist against severe adverse environment regarding high temperature and intense radiation fluxes of different kinds. Despite excellent radiation tolerance, fundamental understanding of radiation damage and defect kinetics is desired for the further improvement and development of radiation tolerant material.

The production rate of point defects in YSZ under irradiation differs in cations and oxygens. Reported defect formation and growth in YSZ is, therefore, dependent on irradiation conditions. The present study investigated the nucleation-and-growth of extended defects in YSZ through *in situ* high voltage transmission electron microscopy under irradiation. Microstructure evolution in pristine and ion-irradiated YSZ was investigated as functions of electron energy and irradiation temperature to gain insights into the kinetic behavior of point defects, under which production rate and mobility of point defects of oxygens and cations change. This dissertation consists of six chapters.

Chapter 1 describes the research goal of this study and step-wise arrangement of the chapters is also outlined.

Chapter 2 reviews theoretical and experimental investigations on radiation damage in ceramics, with an emphasis on fluorite structure oxides. Distinct responses of defect formation under different irradiation particle and temperature are discussed. Elastic displacement cross-section and threshold displacement energies of anion and cation sublattices are also compiled.

In Chapter 3, the basics of transmission electron microscopy (TEM) including imaging and diffraction techniques are firstly described. Experimental details for specimen preparation technique of 8 mol% Y_2O_3 doped zirconia (YSZ) specimen, and ion or electron irradiation conditions are described in detail. *In situ* TEM conditions are also described together with the explanation of data acquisition procedures.

Chapter 4 describes *in situ* TEM results on the nucleation-and-growth of defects in 8 mol% pristine YSZ as functions of electron energy and irradiation temperatures. *In situ* TEM experiments showed that electron irradiation with 1.25 MeV or lower does not induce defect clusters in YSZ. On the other hand, electron irradiation ranging from 1.5 to 3.0 MeV forms oxygen interstitial-type and/or perfect type dislocation loops. The microstructure was developed by the mutual interaction of those defects, and the ratio of displacement damage in oxygen and cation sublattices has found to be a principal factor.

Displacement cross-sections of oxygen and cation sublattices are evaluated by simulations. Threshold displacement energy is also determined experimentally from the energy-dependent microstructure evolution to be around 80 eV for cations.

Chapter 5 presents results on the interaction of Frenkel defects induced by 3.0 MeV electrons with the columnar defects of ion tracks induced by 200 MeV Xe ions. Microstructure evolution was significantly different from pristine YSZ specimens. Ion-tracks are found to act preferential nucleation sites of dislocation loops, and change the nature of dislocation loops and threshold temperature for perfect dislocation formation in ion-irradiated YSZ.

In chapter 6, all the experimental and simulation works done in the wake of this study are summarized as conclusions. Possible directions of research for further understanding of defects' behavior in YSZ are also highlighted.

List of Abbreviations

ABF:	Annular bright-field
BF:	Bright-field
CCD:	Charge-coupled device
DF:	Dark-field
EPR:	Electron paramagnetic resonance
fcc:	Face-centered cubic
FFs:	Fission fragments
HAADF:	High-angle annular dark field
HVEM:	High-voltage electron microscopy
IMF:	Inert matrix fuel
MD:	Molecular dynamics
MSDA:	Multi-step damage accumulation
NPP:	Nuclear Power Plant
PSZ:	Partially stabilized zirconia
RBS/C:	Rutherford backscattering spectrometry/ channeling
SA:	Sudden approximation
SAD:	Selected area diffraction
SOFC:	Solid-oxide fuel cell
STEM:	Scanning transmission electron microscopy
TEM:	Transmission electron microscope
UHVEM:	Ultra-high voltage electron microscopy
XRD:	X-ray diffraction
YSZ:	Yttria-stabilized zirconia

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Chapter 1

Introduction

The important thing is to not stop questioning. Curiosity has its own reason for existence. One cannot help but be in awe when he contemplates the mysteries of eternity, of life, of the marvelous structure of reality. It is enough if one tries merely to comprehend a little of this mystery each day.

*-Albert Einstein
(1879 - 1955)*

Radiation, since its discovery in 1890s, has been used in different aspects of human life including academics, agriculture, medicine, industry, and most importantly for electricity production. As the modern society is going through tremendous scientific and industrial advancements, we are greatly in need of clean, reliable, cheap and uninterruptable source of electricity for sustainable development, and eventually the nuclear power plants (NPPs) became the most preferable option for this. As shown in Figure 1.1, at present about 445 commercial nuclear power reactors are in operation in 31 countries. Moreover, about 64 NPPs are under construction in 15 countries [1]. In NPPs, controlled fission reactions are executed to provide energy indirectly to drive a steam turbine. As high level radioactive materials, such as UO_2 , ThO_2 or PuO_2 , are used as fuel materials, it's obvious that safety and security are the mostly pronounced words in NPP sector. The materials involved in nuclear industry are subjected to severe adverse environment regarding high temperature and intense radiation fluxes

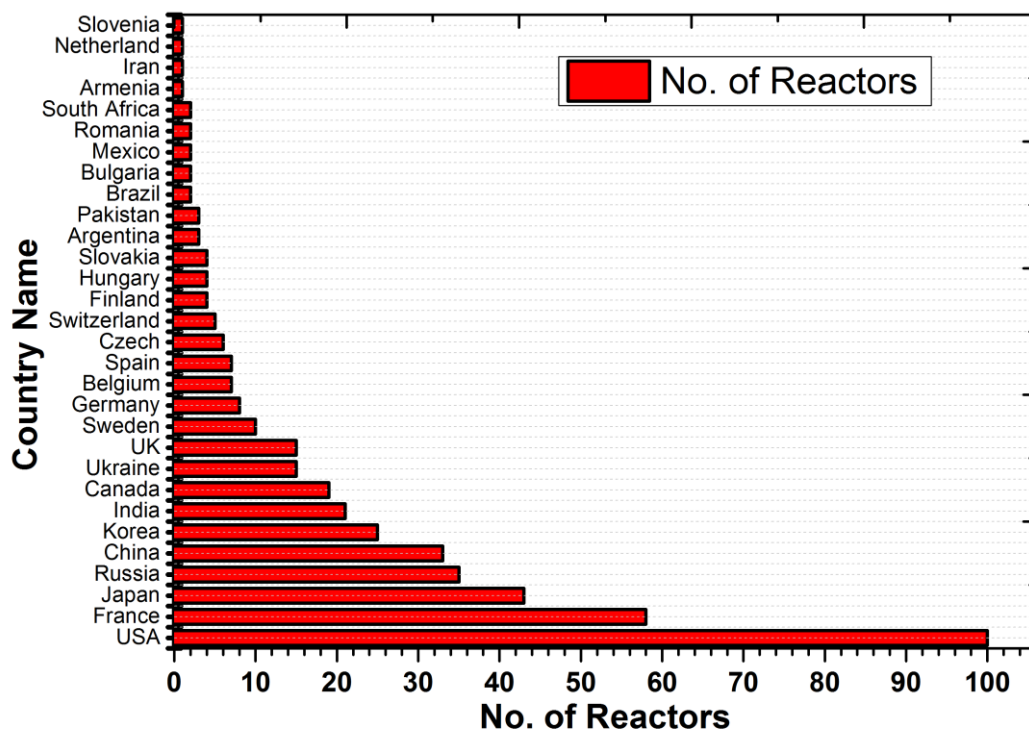


Fig. 1.1: Country-wise total no. of NPP in operation in the world.

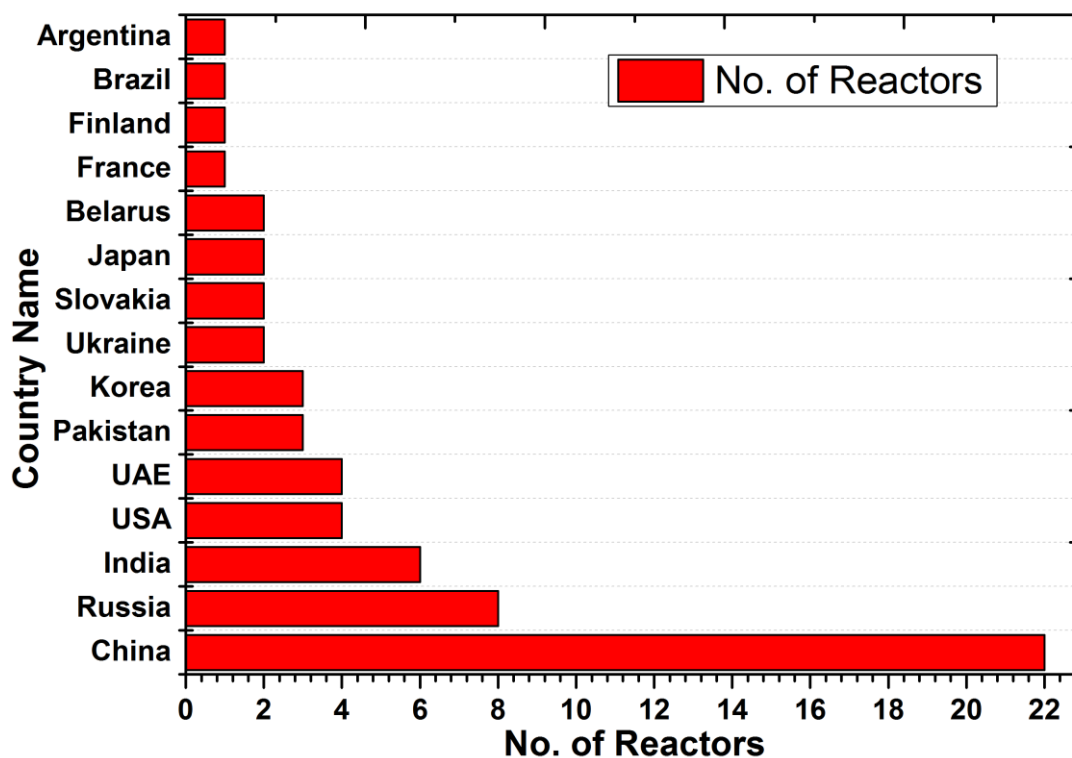


Fig. 1.2: Country-wise no. of NPP under construction in the world.

of different kinds, e.g. energetic fast neutrons and gamma rays, alpha particles, electrons and various kinds of fission fragments [2, 3]. These could degrade the chemical and physical properties of those materials through elastic displacement damage and inelastic electronic excitations. Thus, study of radiation effects in materials including defect nucleation, growth and recovery under severe and complex radiation environment has become of great interest for decades. Furthermore, the future dream for fusion reactors to get cheaper and cleaner energy drives us towards research on the search and development of radiation tolerant materials.

Fluorite structure cubic zirconia (ZrO_2) is one of the most important materials that has received highest attention from researches for years as a solid-state oxygen ion conductor and electrolyte for solid-oxide fuel cells (SOFCs) [4, 5]. Zirconia is of a monoclinic crystal structure at room temperature and it transforms into tetragonal and cubic structures eventually at higher temperatures. Cubic structure zirconia at room temperature can be achieved by substituting Zr^{4+} ions by trivalent cation dopants, such as Y^{3+} ions which induces deficiency of O^{2-} ions in the matrix [6]. The yttria-stabilized zirconia (YSZ) substantially upgrades its chemical, electrical and mechanical properties and most importantly, the presence of extrinsic oxygen vacancies promotes its functionality to use as electrolyte for SOFCs.

The structural vacancies induced by addition of Y^{3+} dopants not only stabilizes ZrO_2

in the cubic form, these vacancies can act as annihilation sites for point defects in radiation environment. Studies show that YSZ is not amorphized under heavy irradiation and for this special characteristics it is considered to be used as diluent for inert matrix fuels (IMFs), which burn plutonium and other actinides instead of uranium which may reduce inventory of actinide in spent fuel. As YSZ is isostructural with UO_2 , ThO_2 and PuO_2 , it could be studied as a surrogate material for evaluating the performance of nuclear fuel and inert matrices at harsh radiation environments [4].

The atomic mass of Zr is much higher than that of O, which led to the higher production rate of oxygen point defects. On the other-hand, migration energies of O vacancy and interstitials are much lower than that of Zr [7]. So in radiation environment, oxygen ion point defects are most likely to form a cluster. Thus, oxygen ion point defects are thought to be largely affect the defect formation behavior. So, the aim of the present study is to understand the kinetic behavior of point defects in YSZ under high energy electron and/or ion irradiation, and for this reason the role of electron energy and irradiation temperature on the evolution of radiation-induced defects, such as dislocation loops, was investigated. Special attention is placed on the difference in the production rate of point defects in anion and cation sublattices in YSZ as well as the difference in the mobility of those point defects. In order to gain fundamental knowledge on the microstructure evolution in fuel exposed by complex

irradiations, microstructure change under electron irradiation was also investigated on ion-irradiated YSZ specimens in advance with swift heavy ions.

This dissertation consists of six chapters. Following the introduction of Chapter 1, theoretical and experimental understandings of radiation effects on YSZ including other nuclear materials were reviewed in Chapter 2, based on review works of extensive experimental and computational studies. Threshold displacement energy, one of the most important parameters in radiation effects, is discussed in detail with some scope to work on in future. The discrepancies in the reported results of temperature effects on radiation damage is also highlighted. It also includes the discussion on structure and stability of YSZ. Chapter 3 discusses the experimental techniques used for this research. Sequential steps of YSZ specimen preparation and experimental (irradiation) conditions are listed in a table also. In chapter 4, nucleation and growth of radiation-induced defects under different electron energy and irradiation temperatures is presented. A threshold temperature for evolution of perfect dislocation loops under electron irradiation is estimated depending on electron energy. Threshold displacement energy for the cation sublattices in YSZ is also bracketed based on HVEM experiments. Chapter 5 shows some preliminary data on the effect of subsequent electron irradiation on ion-irradiated YSZ specimen at different temperature. Defects in low-density core region of ion-tracks are observed carefully

and discussed in comparison with literature. Finally in chapter 6, the main findings of this research with yttria-stabilized zirconia are drawn as conclusions with an outline of future research possibility for understanding further about defect formation mechanism and recovery process.

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Chapter 2

Theoretical and Experimental Background

The saddest aspect of life right now is that science gathers knowledge faster than society gathers wisdom.

*-Isaac Asimov
(1920 - 1992)*

2.1 INTRODUCTION:

Materials are composed of atoms and molecules. Atoms in non-crystals are stacked randomly, whereas the same atomic groups are arranged in a regular manner with periodicity in crystalline solids except for some interruption, such as in grain boundaries and in lattice defects. However, crystals may go through severe structural degradation along with changes in electrical, mechanical and chemical properties in adverse thermal, mechanical or irradiation conditions. This chapter introduces and explains the basics of crystalline solid leading to ceramic materials, radiation defects in various crystals including metals and ceramics, details of defect formation depending on radiation type and irradiation temperatures. It also discusses the reported threshold displacement energies for different cation and anion sublattices of fluorite-type ceramic compounds which is of interest in the present study. Although details of experimental techniques will be described in chapter 3, chapter 2 is concluded with some research questions stating the justification and possible direction of the present research on YSZ.

2.2 CRYSTALS AND CERAMICS:

As mentioned earlier in section 2.1 crystals are solids that maintain a long range order periodically. The crystals are classified into six crystal families and seven crystal systems (Table 2.1) based on reference axes, which have a direction as well as magnitude [1, 2]. The reference axes are labelled as **a**, **b** and **c** and the angles between

Table 2.1: Crystal families and crystal systems

Crystal family	Crystal systems	Axial relationships
Isomeric	Cubic	$a = b = c, \alpha = \beta = \gamma = 90^\circ$
Tetragonal	Tetragonal	$a = b \neq c, \alpha = \beta = \gamma = 90^\circ$
Orthorhombic	Orthorhombic	$a \neq b \neq c, \alpha = \beta = \gamma = 90^\circ$
Monoclinic	Monoclinic	$a \neq b \neq c, \alpha = 90^\circ, \beta \neq 90^\circ, \gamma = 90^\circ$
Anorthic	Triclinic	$a \neq b \neq c, \alpha \neq 90^\circ, \beta \neq 90^\circ, \gamma \neq 90^\circ$
Hexagonal	Hexagonal	$a = b \neq c, \alpha = \beta = 90^\circ, \gamma = 120^\circ$
	Trigonal or	$a = b = c, \alpha = \beta = \gamma$; or
	Rhombohedral	$a' = b' \neq c', \alpha' = \beta' = 90^\circ, \gamma' = 120^\circ$ (hexagonal axes)

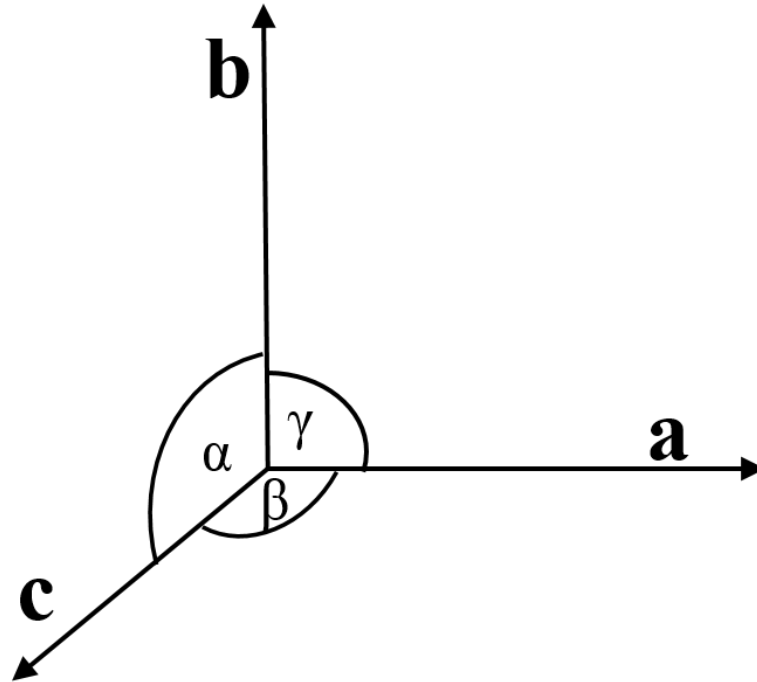


Fig. 2.1: Crystallographic axes **a**, **b**, **c** and the angles between them α , β and γ used to characterize seven crystal systems.

the positive axes are α , β and γ , where α lies between **+b** and **+c**, β lies between **+a** and **+c**, and γ lies between **+a** and **+b** as shown in Fig. 2.1.

Ceramic materials also belong to different crystal systems but are broader in chemical composition than metals with more complicated structures. Usually they contain at least 2 and often 3 or more elements with a combination of stronger bonds called ionic or covalent. These types of bonds cause ceramic materials to possess high elastic modulus and hardness, high melting points, low thermal expansion, and good chemical resistance [3, 4]. As this dissertation is on yttria-stabilized zirconia (YSZ), a fluorite structure oxide ceramic, the structure and stability of zirconia (ZrO_2) and YSZ will be discussed hereupon.

2.3 ZrO₂ AND YSZ: STRUCTURE AND STABILITY:

Zirconia (ZrO₂), the polymorphic oxide ceramic, is a very important material in modern ages for its ability to retain strength and stability at higher temperatures [4, 5]. This high temperature refractory oxide is attractive due to its wide uses in ceramic engineering and as an oxygen sensor in fuel cells, in metallurgy and as thermal barrier coating in engines [6]. Most importantly ZrO₂ has also been reported as one of the most radiation resistant ceramics till now for its excellent radiation stability characteristics and incorporating actinides readily, or higher ability to form solid-state solution in its structure and, hence zirconia has a potential prospect to be used in nuclear industry [7-11].

Zirconia forms a monoclinic structure at ambient pressure up to 1170 °C, tetragonal at temperature between 1170 °C and 2370 °C and cubic at temperatures between 2370 °C and 2680 °C before reaching to its melting point [12]. As tetragonal and cubic phases are unstable at ambient pressure and temperatures, it is stabilized at room temperature by inclusion of oxide dopants such as CaO, MgO and Y₂O₃ [13]. Yttria-stabilized cubic zirconia (YSZ) is formed by adding yttria (Y₂O₃) to zirconia (ZrO₂). In the cubic phase of YSZ, yttrium is replaced to zirconium sublattice of a face-centered cubic (fcc) lattice as solid-state solution, whereas oxygen and structural vacancies exist on a simple cubic anion lattice.

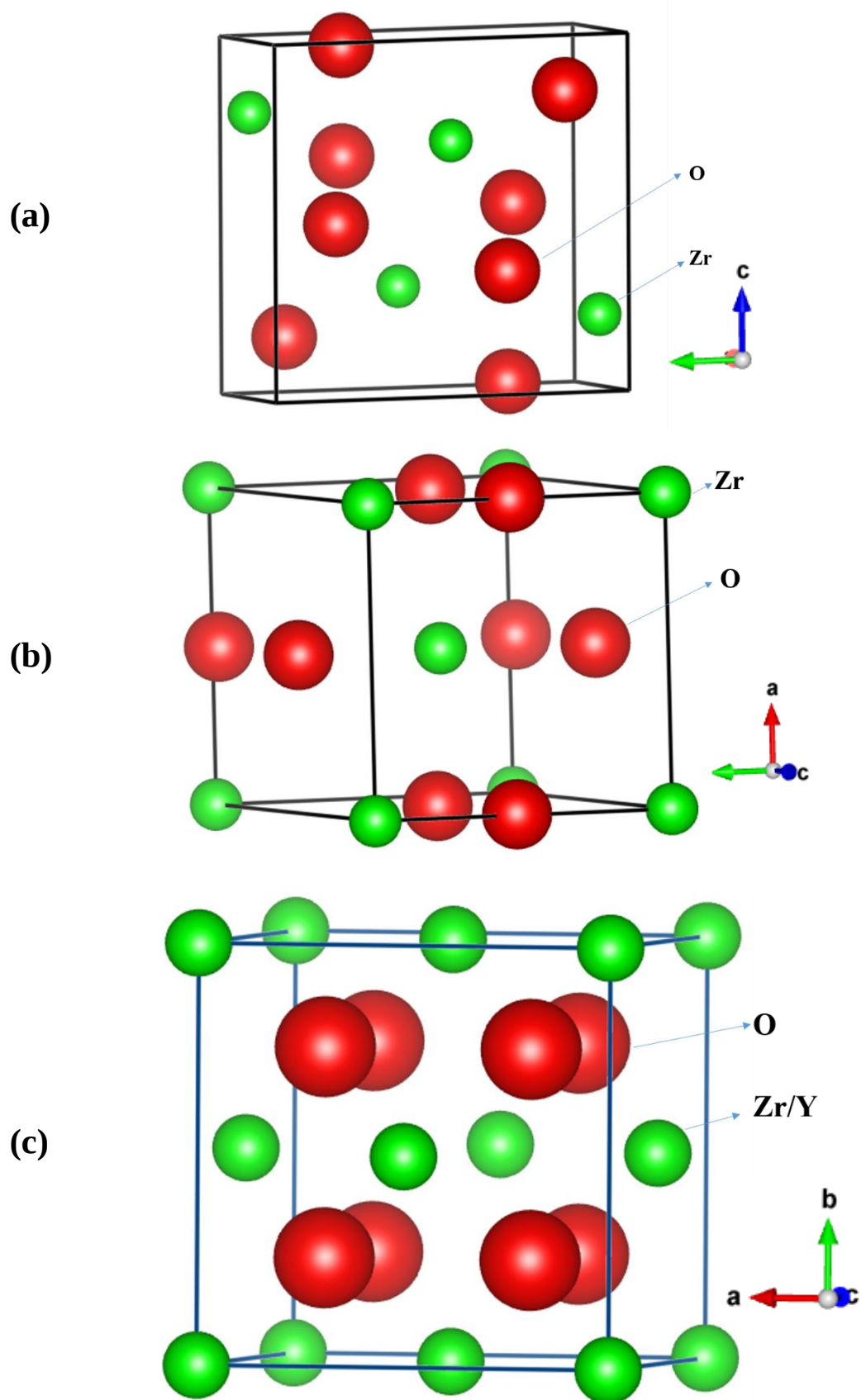
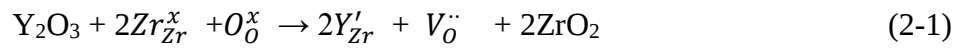


Fig. 2.2: Atomic structure of monoclinic (a), tetragonal (b) zirconia and cubic YSZ (c). Drawn with VESTA (Ver. 3.1.8) software.

Fig. 2.2 shows the atomic structures of zirconia and YSZ at various phases. In the cubic fluorite structure, each cation is located in the center of a cube of eight anions and each oxygen ion or oxygen vacancy is in the center of a cation tetrahedron. One of the most interesting features of stabilizing in the cubic phase of zirconia with yttria is that oxygen structural vacancies ($V_O^{\ddot{}}$) are introduced as follows to compensate charge neutrality [13].



These structural vacancies become mobile at high temperatures effecting the electrical conductivity of the material [14]. Moreover, these can act as annihilation sites for oxygen interstitials induced by radiation. Thus the presence of extrinsic oxygen vacancies in YSZ is supposed to play a role for radiation resistance [14, 15].

Fig. 2.3 presents the Y_2O_3 - ZrO_2 phase diagram [16, 17], where the formation of m- ZrO_2 is seen to a small region at ≤ 3 mol% Y_2O_3 . In the region of 2-6 mol% yttria content partially stabilized zirconia (PSZ) is produced with tetragonal phase and fully stabilized zirconia is seen to form at and above approximately 8 mol%. It is understood from fig. 2.3 that at an yttria content higher than 40 mol%, the system crystallizes as $Y_4Zr_3O_{12}$ [18]. Ionic conductivity of YSZ also exhibits several intriguing features as it increases with dopant concentration up to about 8-9 mol% Y_2O_3 and then shows decreasing trend at higher content of yttria, which is attributed

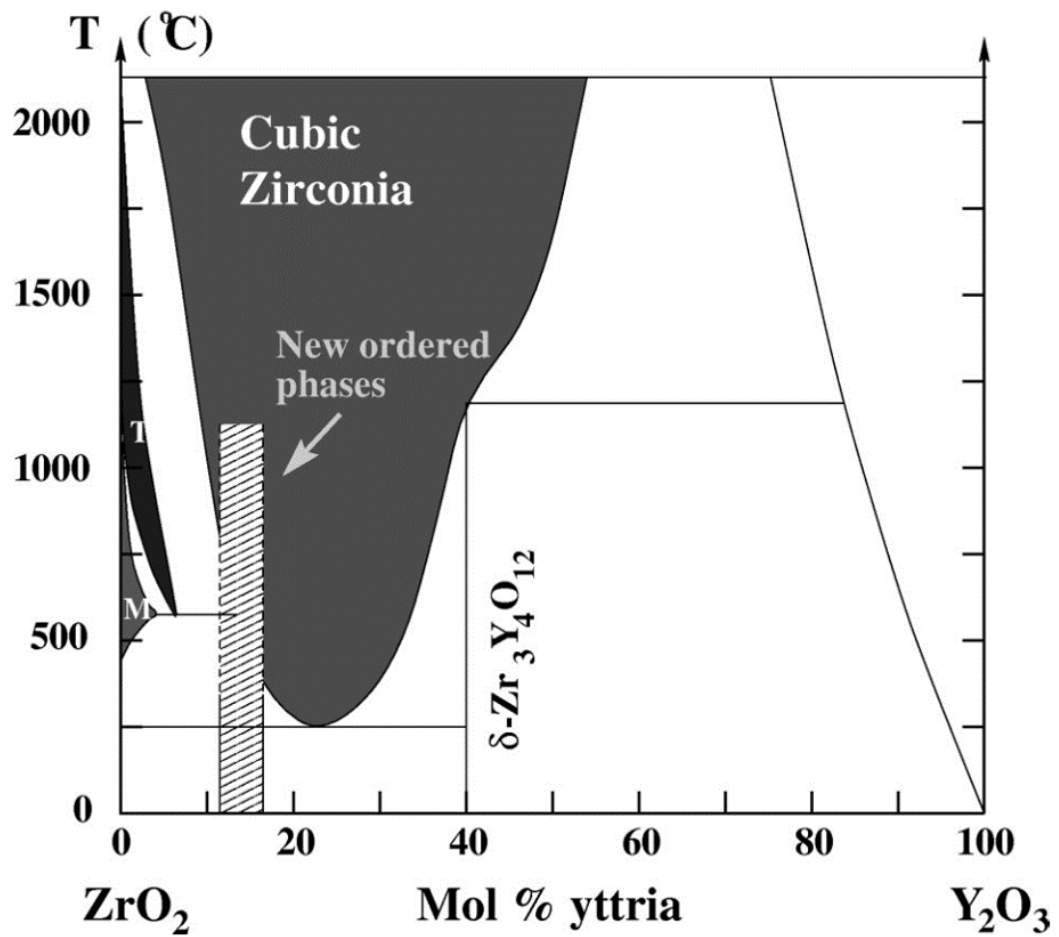


Fig. 2.3: Schematic illustration of the Y_2O_3 - ZrO_2 composition-temperature phase diagram (obtained from Ref. 16 and 17)

to defect interactions, clustering effects and existence of higher number of oxygen vacancies that form ordered arrangements and inhibit the diffusion of oxygen in to vacant sites [19, 20]. The study of YSZ including dependencies on temperature, yttria concentration and manufacturing process have been going on for years. This dissertation concerns with the defect evolution mechanism in 8 mol% YSZ under high energy electron and/or ion irradiation at different temperatures. The oxygen vacancies used in the present specimens (8 mol% YSZ) are, therefore, considered to exist as single vacancies. The theoretical density of YSZ crystal can be calculated as described in the next passage.

2.4 ZrO₂ AND YSZ: THEORETICAL DENSITY CALCULATION:

The theoretical density of YSZ ceramic can be found by calculating the mass of all atoms in the unit cell [1]. The mass of an atom, m_A , is its molar mass (grams mol⁻¹) divided by the Avogadro constant, N_A , (6.02214×10^{23} mol⁻¹).

$$m_A = \text{molar mass} / N_A \text{ (grams)}$$

The total mass of all the atoms in the unit cell is then

$$(n_1 m_1 + n_2 m_2 + n_3 m_3 + \dots) / N_A$$

where n_1 is the number of atoms of type 1, with a molar mass of m_1 , and so on. This can be written as a more compact form as

$$\sum_{i=1}^q n_i m_i / N_A$$

where q is the different atom types in the unit cell. The density, ρ , is simply the total mass divided by the unit cell volume, V (cm³):

$$\rho = \{ \sum_{i=1}^q n_i m_i / N_A \} / V \quad (2-2)$$

Here the theoretical density of 8 mol% YSZ is calculated to be 6.018 cm⁻³ according to equation 2.

As the research goal of this dissertation is to gain insights into the effect of irradiation temperature and electron energy on the evolution of dislocation loops in YSZ, now I will discuss on the theoretical and experimental research works done on radiation effects with YSZ along with comparison with other metals and ceramic materials and, eventually the remaining research question along with future implication of my research plan will be addressed.

2.5 RADIATION DAMAGE IN MATERIALS:

Zirconia is one of the paramount research materials for decades and the reasons for this are described briefly in earlier sections. I will discuss the justification of its getting priority here in detail. It is needless to say the necessity for the development of radiation tolerant materials due to a number of reasons, such as proliferation resistance, energy security, encapsulation of radioactive wastes and

nuclear energy partnership [13, 21]. Newer type of fuel for advanced nuclear reactors are in discussion named ‘inert matrix fuels (IMF)’ [7, 11, 22, 23], which burn plutonium or other actinides such as americium instead of uranium. Zirconia is one of the most potentials candidates for use as a non-fertile diluent for IMFs due to its chemical durability and exceptional radiation tolerant characteristics. When Zr^{4+} is substituted by aliovalent cations such as Y^{3+} , it stabilizes at cubic form with fluorite structure at room temperature. As this YSZ is isostructural with compounds such as Urania (UO_2), plutonia (PuO_2), ceria (CeO_2) and thoria (ThO_2), it is of great concern in nuclear industry [24, 25]. Practically YSZ, as a fuel matrix should uphold against high level and different kinds of radiation exposure including fast neutron, gamma- and beta-rays, fission fragments, and self-irradiation from alpha decay of Pu and other actinides, which may degrade its chemical, mechanical and thermal properties. The radiation defects induced by those radiations may vary depending on irradiation dose, temperature, pressure, sintering process which influence stoichiometry of the compounds, and so on.

A radiation experiment at 800 °C with xenon ion irradiated CeO_2 , as a surrogate material to UO_2 , up to 5×10^{15} ions/cm² shows that formation and growth of defect clusters including dislocation loops and cavities is a function of increasing atomic displacement dose [26]. On the other hand, electron-irradiation subsequent to

ion-irradiation in YSZ shows the production of anomalous large defect clusters which possess strong stress-strain fields and significantly different contrast from perfect dislocation loops with stoichiometric composition. Furthermore, the extended defects later become unstable after reaching to a critical size and multiply dislocation network as shown in Fig. 2.4 [27]. The critical size for the transformation of the defects is reported elsewhere to be 1.0-1.5 μm in diameter and the loops are discussed as oxygen interstitial-type dislocation loops (Fig. 2.5) [28, 29]. However, these anomalous large defect clusters are not seen when YSZ was irradiated solely with ions.

Recent studies on YSZ mostly emphasize on assessment of defect evolution in the matrices with different species of ion irradiation at various doses and different irradiation temperatures. Solely 60 keV xenon ions irradiation of YSZ at very high flux (5×10^{12} ions/cm².s) induces no amorphization from ambient to very high temperatures as 1073 and 1473 K, but forms bubble and dislocation loops, while dependence of loop formation on ion species at high temperatures is also observed after irradiation with helium ions [30]. Similar non-amorphizability along with phase stability of YSZ are reported in other ion irradiations with energies ranging from several tens keV to a few MeV [10, 31-35]. Zirconia has shown to keep cubic crystal structure under cryogenic and ambient temperature irradiation conditions at a very high displacement damage level of 100 dpa [31-33], which is much higher value than

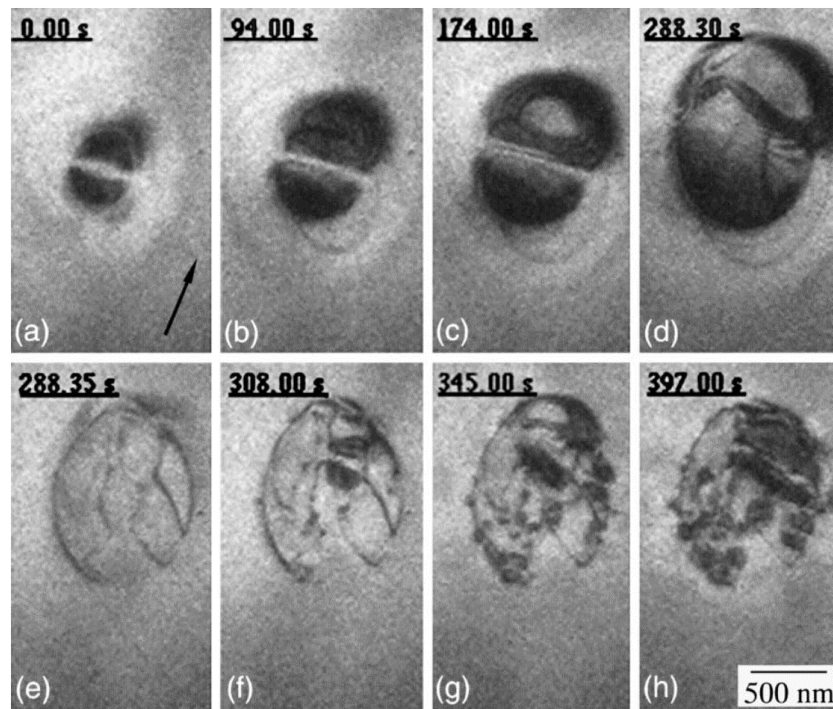


Fig. 2.4: the growth of defect clusters under 200 keV electron irradiation at 470 K. The sample was irradiated originally with 300 KeV O^- ions at 470 K to a fluence of $5.1 \times 10^{17} O^+/m^2$ (Obtained from ref. 27).

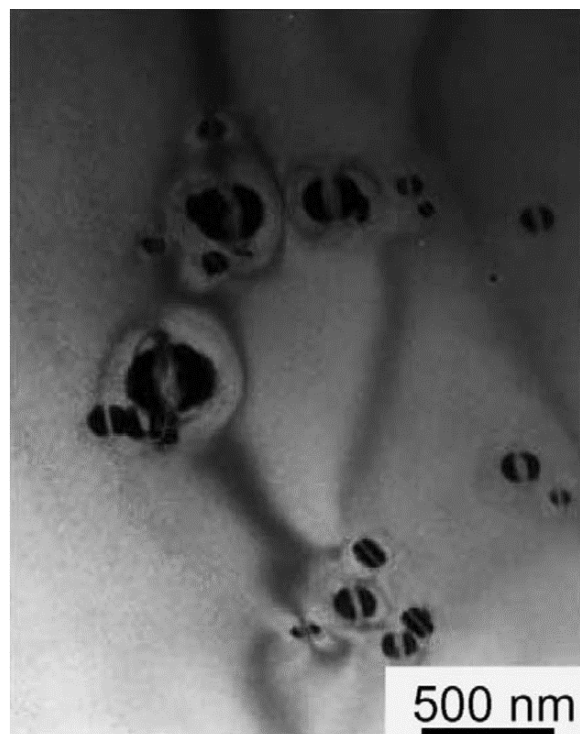


Fig. 2.5: Extended defect clusters formed in YSZ around a focused electron beam of 200 keV with a beam diameter of $\sim 1 \mu m$. The specimen was irradiated at 470 K with 300 keV O^+ ions to $5.1 \times 10^{17} m^{-2}$ followed by 200 keV electrons at 370 K for 210 s with an e^- flux of $1.3 \times 10^{23} m^{-2}s^{-1}$ (Obtained from ref. 28).

that necessary dose (25 dpa) to amorphize magnesium aluminate spinel (MgAl_2O_4) [34].

Irradiation experiments with different ions were also reported in the interest of knowing about the fission fragment damage at real nuclear environment. 72 MeV I^+ ion irradiation with a fluence of $1.0 \times 10^{19} \text{ m}^{-2}$ and irradiation temperature ranging from 300 to 1770 K shows significant microstructural changes to the crystal [35]. A three-step damage accumulation process following (i) an isolated defect cluster stage (stage I), (2) a transition stage in which damage increases rapidly over small range on ion doses (stage II), and (3) a saturation stage in which damage accumulation is retarded or increases only slowly (stage III), was reported in Xe-irradiation experiments on YSZ [7]. Jagielski et al. [36] later gave a phenomenological description of the damage accumulation (MSDA (Multi Step Damage Accumulation) model) occurring during ion irradiation of crystalline solids, where they postulated that the damage accumulation process occurs at several steps, each step being triggered by destabilization of the current structure. This model also supports the findings of 500 keV Xe- irradiated CeO_2 at 800 °C, where the nucleation of dislocation loops was completed at early stage of irradiation and with increasing dose the dislocation loops expanded rapidly and began to interact with each other, finally tangled dislocation network had evolved [26]. It is also reported by Yang et al. [37]

that under swift-heavy ion irradiation, high electronic excitation energy, S_e causes recovery of defects and promotes formation of extended defects. Ion beam irradiation using charged particle accelerators were used to reproduce the irradiation conditions encountered practically in nuclear reactors [38]. Irradiation with swift heavy ions (in the hundred MeV range) in oxide ceramics produces overlapping of ion tracks at very high doses and lead to the formation of nanometer-sized domains (~ 50 nm) characterized by a slight misorientation with respect to the main crystallographic sample orientation [39-41] and TEM observations [44]. Previous studies on ion tracks in fluorite-structured oxides such as ZrO_2 , CeO_2 and UO_2 show that the ion tracks in such regions are not amorphized [35, 39, 42-45]. But the atomic density in core damaged regions, with a diameter of 3-4 nm, was reported to decrease by about 13%, suggesting the formation of vacancy and/or small vacancy clusters at the core regions of ion tracks with generation of interstitial ions in the surrounding regions [46]. It is, therefore, important to study the defect formation and interaction irradiated with different radiation sources, such as electron irradiation on YSZ irradiated with heavy-ions in advance. This may lead to interesting outcomes for actual radiation environment where a number of radiation type and range of energy are employed.

In the case of electron irradiated metals and ceramics, the interference of electron with the atomic sublattices cause a change with displacement damage and it

is dependent on the electron density passing through the crystal [47]. Vacancies and interstitials are continuously produced with a proportion of the product of irradiation flux and displacement damage cross-section [48]. In the very early stage of irradiation at low temperatures, the concentration of vacancies and interstitials increases proportionally with irradiation fluence. In a thin foil condition, interstitial atoms rapidly escape to the surface sink with its higher migration rate, while in a thicker specimen condition, interstitials may reach the critical concentration to form interstitial clusters, generally in the form of dislocation loops [49]. Under irradiation at higher temperatures, both vacancies and interstitials have enough mobility. Similar to the low temperature case, interstitial clusters may form and these clusters may absorb vacancies along with vacancy-interstitial mutual annihilation. In the case of ceramic materials such as YSZ, multiple atomic species are involved with different values of migration energy of vacancies and interstitials which are described in Table 2.2. Thus different irradiation conditions, such as with different irradiation energy and irradiation temperature, they (vacancies and interstitials of the different atoms) may respond differently resulting formation of distinct type of defect clusters.

Fig. 2.6 shows the temperature dependence of the growth behavior of dislocation loops with respect to the migration energies of vacancies for several materials [50]. So, it is much clear from above discussion and Table 2.2 that irradiation

temperature may greatly influence the defect formation behavior in YSZ. In the next section, reported results on the defect kinetics and microstructure evolution with respect to irradiation temperature dependence and I will highlight the point of discrepancies.

Table 2.2: Migration energies of vacancies and interstitials of different atomic species in YSZ [51].

	Zr ion (Cation)	Y ion (Cation)	O ion (Anion)
Vacancy migration energy (eV)	6.2	-	0.3
Interstitial migration energy (eV)	5.9	6.6	0.7

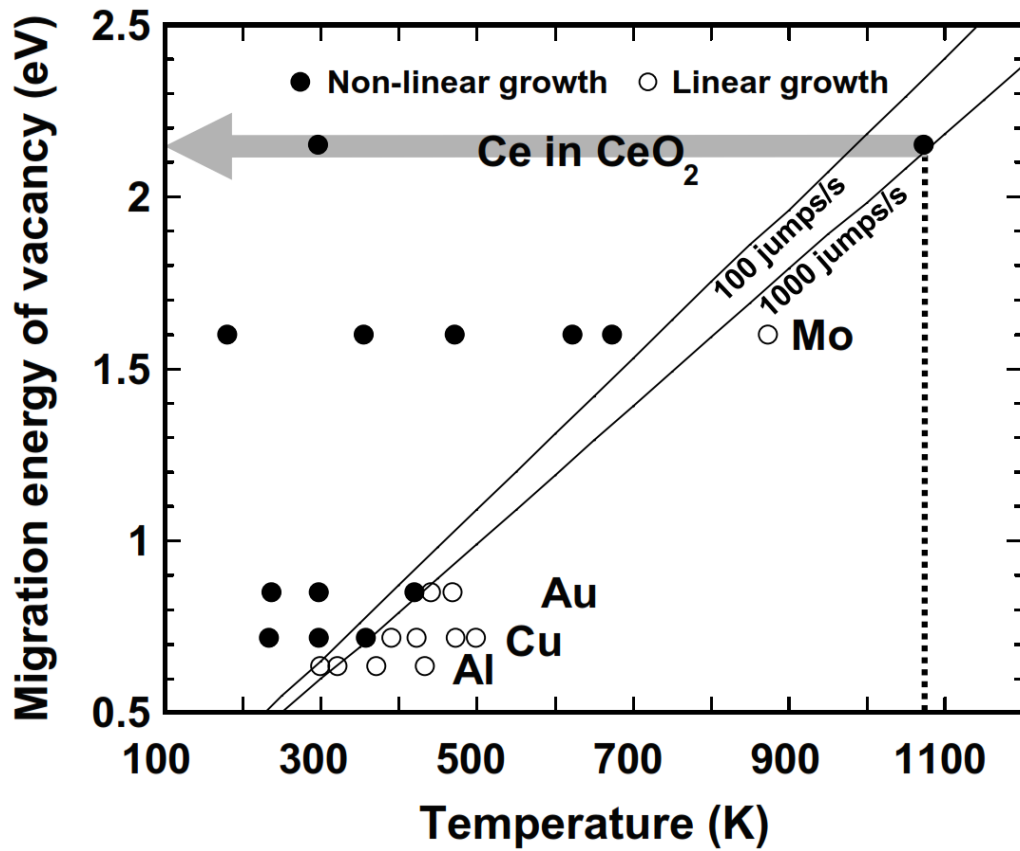


Fig. 2.6: Temperature dependence of the growth behavior of dislocation loops with respect to the migration energy of vacancy for several materials (Obtained from ref. 51).

2.6 TEMPERATURE DEPENDENCE OF RADIATION DEFECTS:

To study the migration behavior, or the recovery stage of point defects, materials should be irradiated at a temperature close to liquid He (4.2 K), and then temperature should be raised for annealing in a temperature controlled system [52]. Annealing Cu specimens irradiated with electrons over a very wide range, from 14 to 600 K, gives a several sub-stages (recovery stage) and migration energy of point defects, where properties and behaviors are different as summarized in ref. [52] (shown in table 2.3)

Table 2.3: Recovery stages in electron irradiated Cu (obtained from ref. [52]).

	Ia	Ib	Ic	Id	Ie	II	III	IV	V
Approximate temperature (°K)	16 (1)	28 (1)	32 (1)	39 (1)	53 (1)	not in pure Cu (1)	300 (7, 8) 235 (4)	350-600(7)	
Activation energy (eV)	0.050 (1)	0.085 (1)	0.095 (1)	0.12 (1)	0.12 (1)	—	0.60 (4, 7)	—	—
Order of reaction (x)	1 (1)	1 (1)	1 (1)	1 (1)	2-3 (1, 2)	—	2 (7)	—	—
Number of jumps (j)	1 (1)	1 (1)	1 (1)	10 (1)	10 ⁴ (1)	—	10 ⁸ (7)	—	—
Effect of increased dose			none (1)		reduces temp. (1)	—	—	—	—
Effect of increased impurity		small reduction (1, 5)		large reduction (1, 5)		introduces peaks (8)	affects magnitude (8)	—	—
Effect of increased electron energy	increase (1, 3)	reduction (1, 3)		increase (1, 3)		—	—	—	—
Change in dislocation pinning due to stage			none (4, 6)		increase (4, 6)	—	decrease (9)	—	—
Percentage recovery of resistivity		90 % (1, 2)			—	9 % (1, 2)	1 % (1, 2)	—	—

(1) Corbett *et al.* see review by Walker (1962)
(2) Meechan, Sosin & Brinkman (1960)
(3) Sosin (1962a)
(4) Sosin (1962b); Keefer & Sosin (1964)
(5) Sosin & Neely (1962)

(6) Lomer (1963)
(7) Meechan & Brinkman (1956)
(8) Martin (1961)
(9) Keefer & Sosin (1964)

M. Kiritani *et al.* [49] also investigated the formation and growth behavior of interstitial-type dislocation loops in Al, Au, Cu, Fe and Mo by electron irradiation in a high voltage electron microscope and showed that the growth speed of interstitial loops is controlled by the migration rate of vacancies but not by that of interstitials, but the growth speed of loops in a thin specimen is directly proportional to the irradiation intensity and does not vary with irradiation temperatures.

Irradiation experiments with 4 MeV Au⁺⁺ ions [53] in a broad fluence range

(5×10^{12} to 2×10^{16} cm^{-2}) and at five irradiation temperatures: 80, 300, 573, 773, and 1073 K show that, whatever is the irradiation temperature, the damage build-up follows a multi-step process, with no enhanced dynamic annealing process. But an accelerated transitions in the damage accumulation process is observed with increasing irradiation temperatures (Fig. 2.7). In contrast, in the case of other ceramic oxide such as SrTiO_3 [54] or MgO [55], dynamic annealing process is found dominating at increasing irradiation temperatures. A strong temperature dependent damage build-up is also reported by Moll et al. [56], in which the fluence showing rapid increase of damage fraction shifts towards lower fluence with increasing temperature.

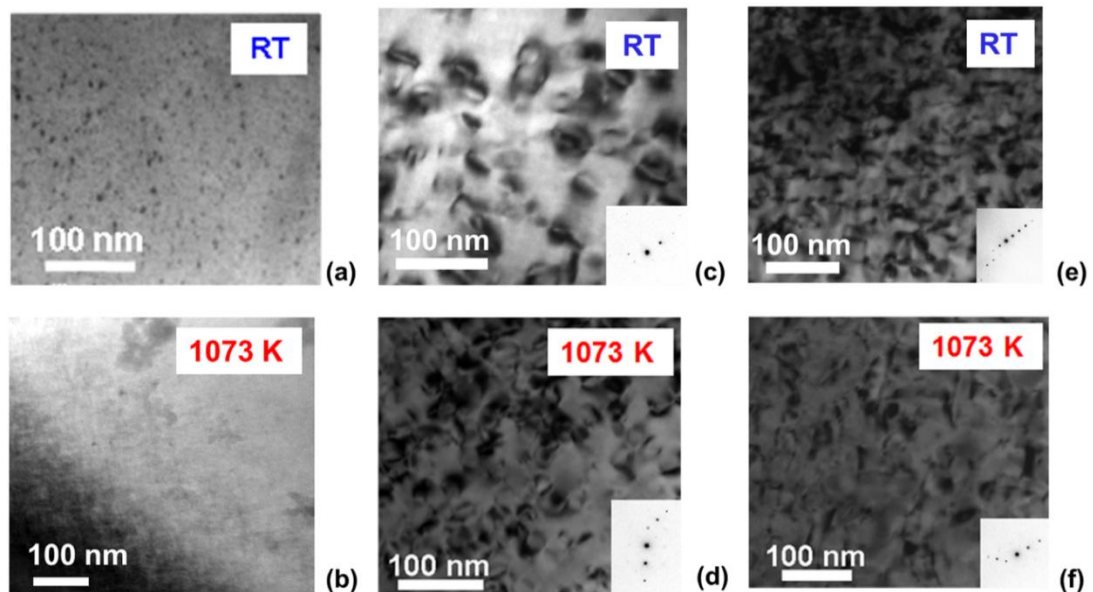


Fig. 2.7: TEM bright-field micrographs recorded in YSZ crystals irradiated with 4 MeV Au^{++} ions at 300 K (top) and 1073 K (bottom) and at different places (fluences) of the damage build-up: (a) 10^{15} cm^{-2} and (b) $5 \times 10^{13} \text{ cm}^{-2}$ correspond to the first step; (c) $1.5 \times 10^{15} \text{ cm}^{-2}$ and (d) $4 \times 10^{14} \text{ cm}^{-2}$ are characteristic of the beginning of the second step; (e) $2 \times 10^{15} \text{ cm}^{-2}$ and (f) $7 \times 10^{14} \text{ cm}^{-2}$ illustrate microstructure observed at the end of second step (Obtained from ref. 53).

2.7 DISPLACEMENT CROSS-SECTION (σ_d) AND THRESHOLD DISPLACEMENT ENERGY (E_d):

Electrons, provided by transmission electron microscopes, in the energy range of MeV have been frequently used to irradiate materials in the study of radiation damage, because it has dual advantage of producing simple type of damage, that is Frenkel defects, than heavy particles such as neutrons or heavy ions [57], and can record and observe *in situ* the radiation damage simultaneously [50]. In order to calculate the probability of displacing an atom in a material from its lattice position by fast electron, it is necessary to know the scattering cross-section between an electron and an atom in the target material. The electrons used in radiation damage experiments are in the relativistic velocity range, and Mott [58-60] has expressed the scattering between a point nucleus and an electron as an infinite series of Legendre expansion. Later McKinley et al. [61] simplified the Legendre expansion and evaluated the cross-section for Coulomb scattering of relativistic electrons by atomic nuclei, the most frequently used as McKinley-Feshbach formula, as follows [57]:

$$\sigma_{\text{tot}}(E, T_d) = \frac{\pi Z^2 e^4 (1-\beta^2)}{m^2 C^4 \beta^4} \left\{ \int_{T_d/T_m}^1 \frac{dx}{x^2} M(x, E) \right\} \quad T_d \leq T_m \leq 2T_d \quad (2-3)$$

$$= \frac{\pi Z^2 e^4 (1-\beta^2)}{m^2 C^4 \beta^4} \left\{ \int_{T_d/T_m}^{2T_d/T_m} \frac{M(x, E)}{x^2} dx + \int_{2T_d/T_m}^1 \frac{T_m}{2T_d} \frac{M(x, E)}{x^2} dx \right\} \quad (2-4)$$

$$T_m \leq 2T_d$$

Where E is the kinetic energy of the electron, M is the mass of the target atom, T_m is the maximum transferred energy, T_d is the threshold displacement energy to displace an atom from its lattice site (The notation of E_d is used for describing threshold displacement energy later on), $\beta^2 = E(E+mc^2) / (E+mc^2)^2$, Z is the atomic number of the target nucleus, e is the electronic charge and $M(x, E)$ is the ratio of the Mott to Rutherford cross-section, which calculated using method of Doggett and Spencer [62].

In recent days, a computer code named SMOT/POLY code is used that calculates scattering cross-section, σ_d versus electron energy for a given T_d value [63]. This code is especially devised for polyatomic targets, where the total cross-sections include a major contribution of the primary elastic collisions and a minor one of the secondary collisions with small collision cascades [64]. Cross-section data from this code is consistent with those recently used for YSZ irradiations in a 1 MeV high voltage electron microscope [28], with reference to the well-known Oen's charts [57].

After the above discussion on scattering cross-section, it is clear that the most important physical parameter for describing radiation damage in a material is the threshold displacement energy, E_d , which is the minimum amount of kinetic transferred energy to a lattice atom that results in the formation of a stable Frenkel pair [65]. In ceramics, such as YSZ, the crystal structures consists of multiple sublattices, so this parameter must be separately measured or computationally

determined for each sublattice and for each crystallographic direction since the displacement energy is dependent on the crystallographic orientation [66]. A number of theoretical and experimental procedures have been used until now to evaluate E_d values for different atomic sublattices in metals and ceramics. In most of the threshold displacement energy measurements electron irradiation sources are used to produce isolated Frenkel defects, whereas some studies used optical spectroscopy or EPR techniques to uniquely monitor the behavior of a particular type of defects such as anion vacancies [64, 65, 67]. However, it has been reported that the EPR or optical signals may not be visible unless displacement damage occurs on both sublattices [68]. Theoretically, the threshold displacement energies can be calculated by applying sudden approximation (SA) method [69] within the classical Mott-Littleton [70] approximation or by molecular dynamics (MD) method [71]. In recent years, *ab initio* molecular dynamics methods in which the forces acting on the nuclei are calculated by electronic structure calculations rather than empirically fitted potentials have proved to be a valuable tool for gaining insight on defect configurations produced by low-energy recoil events with *ab initio* accuracy [66, 72-74].

It is generally assumed in TEM studies that recognizable damages require displacement defects from all of the sublattices. Hence, the measured threshold electron energy for creation of damage generally corresponds to the minimum energy

to displace the most massive atomic species or the highest E_d species in the ceramic.

So the threshold displacement energy, E_d , can be bracketed by the following well-known equation [65, 75].

$$E_d = \frac{2E_e(E_e + 2m_e c^2)}{m c^2} = \frac{2147.7 E_e (E_e + 1.022)}{A} \quad [\text{eV}] \quad (2-5)$$

Where E_d is in eV, E_e is the incident electron energy in MeV and A is the atomic mass of the displaced ion in the right side of equation 5. However, in some ceramic materials, there exist structural vacancies or empty interstitial sites either in the oxygen sublattice (ex. YSZ) or in cation sublattice (ex. MgAl_2O_4). For this reason, displaced ions may spontaneously recombine with structural vacancies. Furthermore, the different values of E_d lead to the non-stoichiometric defect clusters, instead of stoichiometric one. Aggregation of displaced point defects is dependent on the materials, and thereby the evaluation of E_d has not been fully achieved at this moment, and a wide range of values are reported in literature for fluorite oxides, such as UO_2 , ThO_2 , CeO_2 , ZrO_2 , and YSZ, based on experimental and theoretical calculations (Table 2.4). It is, therefore, very important to estimate threshold displacement energy, E_d for Zr and O sublattices in YSZ in a well-defined experimental technique.

Table 2.4: Threshold displacement energies for different atomic species in different fluorite structure oxide ceramics

Material	Threshold displacement energy, E_d (eV)		Method	Reference
	Cation	Anion		
	~ 40	~ 20	HVEM	[76]
UO ₂	35 - 51	-	MD Simulation	[77]
	43 - 85	16 - 28	MD Simulation	[78]
ThO ₂	48.5 – 61.5	17.5 - >100	<i>ab initio</i> MD	[66]
	44 ≪ 58	<33	HVEM	[50]
CeO ₂	56	27	MD Simulation	[71]
	46 - 63	20 - 33.5	<i>ab initio</i> MD	[66]
ZrO ₂	54 - 68.5	14 - >100	<i>ab initio</i> MD	[66]
YSZ	80	120	EPR	[64]
	80	>200	MD Simulation	[67]

2.8 CONCLUSIONS:

YSZ is a material of interest in nuclear industry for a number of reasons. The mechanism of defect evolution at various irradiation conditions in this material is not fully understood yet. So, the goal of this dissertation is to unfold some important issues, such as:

- Effect of selective displacement damage of oxygen and/or cation in YSZ under high energy electron irradiation.
- Role of electron energy and irradiation temperature in defect formation behavior.
- Estimating E_d for displacement damage on oxygen or cation sublattices, and unmasking the interaction of ion-tracks with high energy electron irradiations.

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Chapter 3

Experimental Details

Dream is not that which you see while sleeping, it is something that does not let you sleep.

-A. P. J. Abdul Kalam
(1931 - 2015)

3.1 INTRODUCTION:

The transmission electron microscope (TEM) has become a very powerful tool for microstructural characterization of materials. Besides diffraction and spatial imaging, the high-energy electrons in TEM can cause elastic displacements of the atoms and electronic excitations in the specimen, thus leading it to one of the ideal tools to produce radiation damages in the material and to observe the damage process simultaneously as well. This dissertation covers nucleation and growth of radiation damages on pristine and ion-irradiated YSZ at different electron energies and irradiation temperatures. The theoretical and experimental background of this research topic and the material of interest, YSZ, have been described in the earlier chapter. This chapter will cover the basics of TEM, the specimen preparation procedure and the experimental technique/condition used for data acquisition.

3.2: TRANSMISSION ELECTRON MICROSCOPY:

A schematic diagram (Fig. 3.1) [1] is presented here to show the components of TEM. A high energy beam of electrons is allowed to pass through a thin specimen

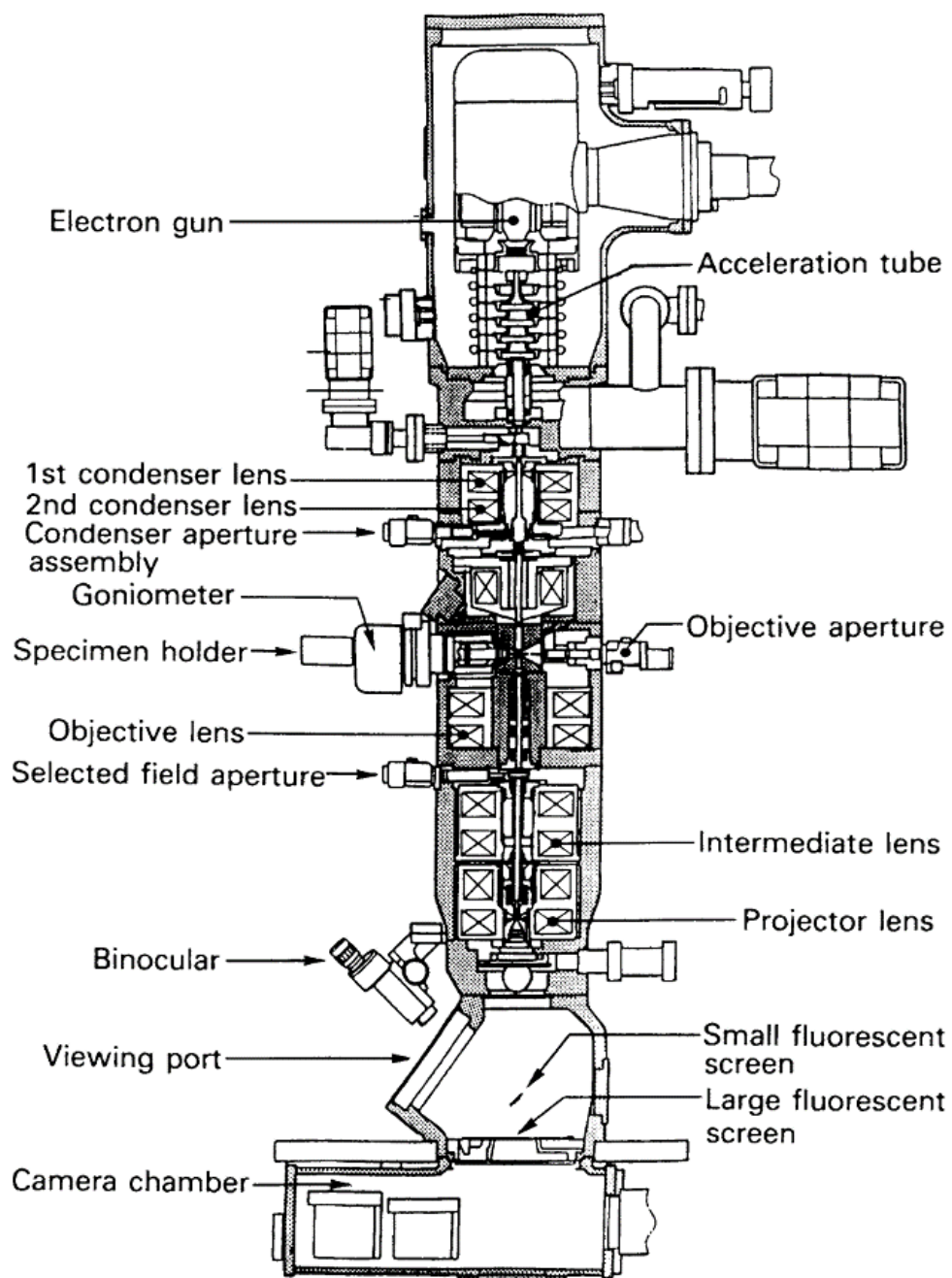


Fig. 3.1: Schematic illustration of typical TEM with its components. (Obtained from Ref. 1)

and the interactions between the incident electrons and the nuclei of atoms and surrounding orbital electrons can be used to observe features such as the crystal structure, features in the microstructure like dislocations, chemical and elemental analysis, and so on. TEM has the same basic principles as the optical microscopes but uses electrons instead of light. The achievable resolution for a wavelength λ is given by the diffraction limit δ [2] as:

$$\delta = 0.61 \frac{\lambda}{NA} \quad (3-1)$$

with numerical aperture NA , which can be approximated by the angle of incidence $NA \approx \alpha \approx r_a/r_{wd}$, where r_a is the radius of the objective lens aperture and r_{wd} is the working distance. Optical microscopes can reach to a resolution of $\delta = 200$ nm, but as the wavelength of electrons is much smaller than that of light, the optimal resolution achievable for TEM images is many orders of magnitude better than that of from a light (optical) microscope. The TEM system uses electrical and magnetic fields to control the electron beam. The law of refraction in optics is exchanged with Lorentz force in electrodynamics but the electron optical system has similar diffraction limits as optical system, because they depend on wave nature of electron beam [3]. The de Broglie wavelength λ of an electron with momentum p is given by

$$\lambda = \frac{h}{p} = \frac{h}{\sqrt{2m_e E_b}} \quad (3-2)$$

here h is Planck's constant. The electron has a rest mass m_e and energy, $E_e = m_e c^2 =$

511 keV. If an electron with charge q_e is accelerated from rest by an electrical potential U , to the electron beam energy $E_b = q_e U$, it will have a wavelength of 1 nm at 1 eV decreasing to 1 pm at 100 keV where it will be travelling with 50% of the speed of light.

The conventional bright-field (BF) and dark-field (DF) imaging techniques as well as weak-beam dark-field imaging are used for this research work. Fig. 3.2 shows the ray's path in the image modes to form BF and DF images. The image found in TEM study is formed by electron rays passing through the specimen. Instead of glass lenses, the TEM uses electromagnetic lenses to focus the electrons into a very thin beam. Depending on the density and thickness of the specimen, a part of the electrons are scattered and are interrupted by apertures inserted in the path of the electron beam. At the bottom of the microscope the un-cutted electrons hit a fluorescent screen and/or a detecting camera such as a CCD camera, which allow to form a shadow image of the specimen with its different parts displayed in varied darkness according to the electron intensity. It is noted here that all of the rays in the back focal plane is not necessary to form an image, rather a full image can be formed with only those rays passing through one point in the back focal plane. An image made with only those electrons that have been diffracted by a specific angle can be achieved by using an objective aperture at a specific location in the back focal plane. Thus, when the

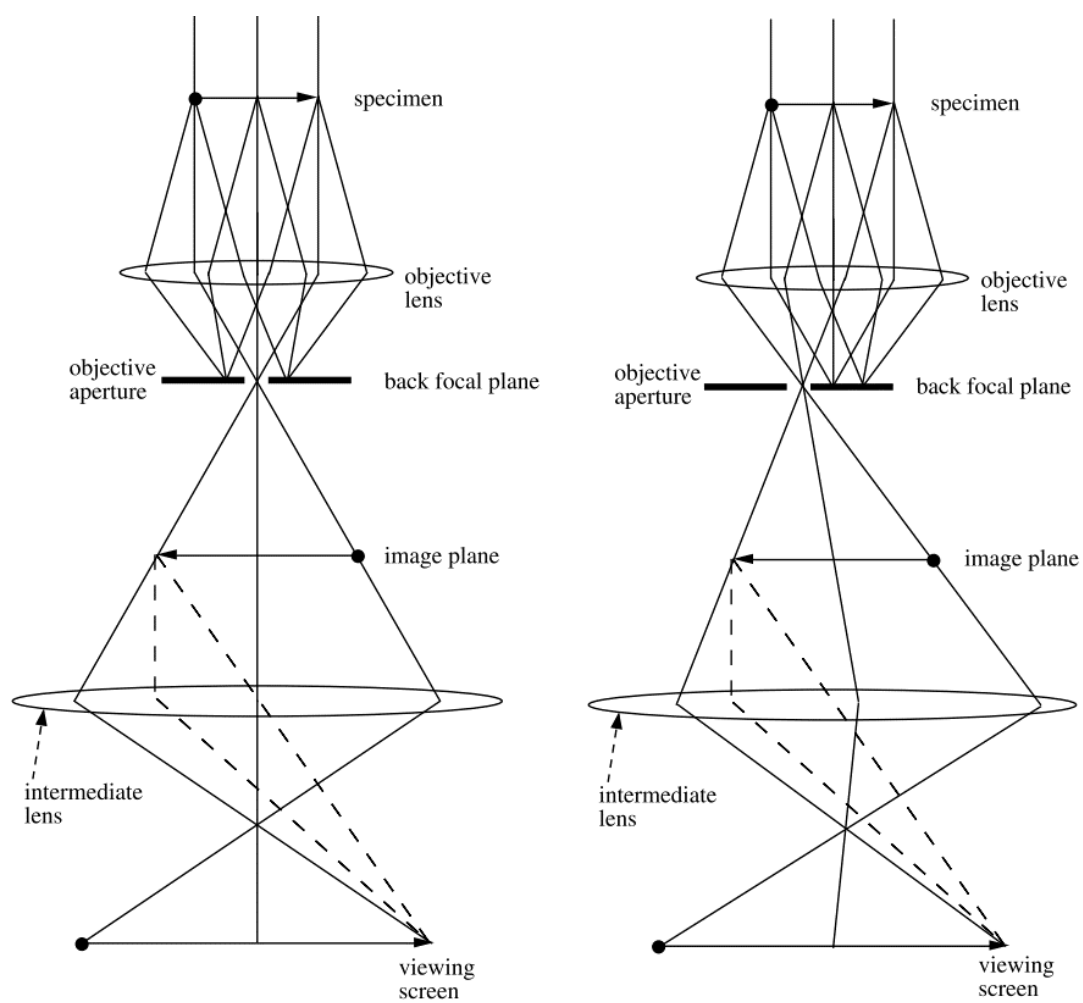


Fig. 3.2: Ray path diagram of image formation in bright-field, BF (left) and dark-field, DF (right) mode (obtained from ref. 1).

aperture is positioned to pass only the transmitted electrons, a bright-field (BF) image is formed, whereas a dark-field (DF) image is formed when the aperture is positioned to pass only some diffracted electrons. The features in an image originate from the diffraction contrast which is the variation in intensity of electron diffraction across the specimen. This diffraction contrast is achieved by inserting an objective aperture in the beam. In the microscope, typical objective apertures range from 0.5 to 20 μm in diameter. The apertures are movable with high mechanical precision, and can be positioned around selected diffractions in the back focal plane of the objective lens. In the diffraction mode, the image of both the diffraction pattern and the aperture are visible on the viewing screen, and the objective aperture can then be moved until it is in the desired position. When the objective aperture is positioned properly, the microscope is switched back into image mode, and either a dark-field or a bright-field image is formed.

A second aperture named 'intermediate aperture' is positioned in the image plane of the objective lens to confine the diffraction pattern to a selected area of the specimen. This technique is called 'selected area diffraction (SAD)'. The SAD pattern that appears on the viewing screen originates from the area of the specimen selected in the image mode. The separation of the diffraction spots found in the SAD pattern can be used to determine the interplanary spacings in crystals. This technique is also

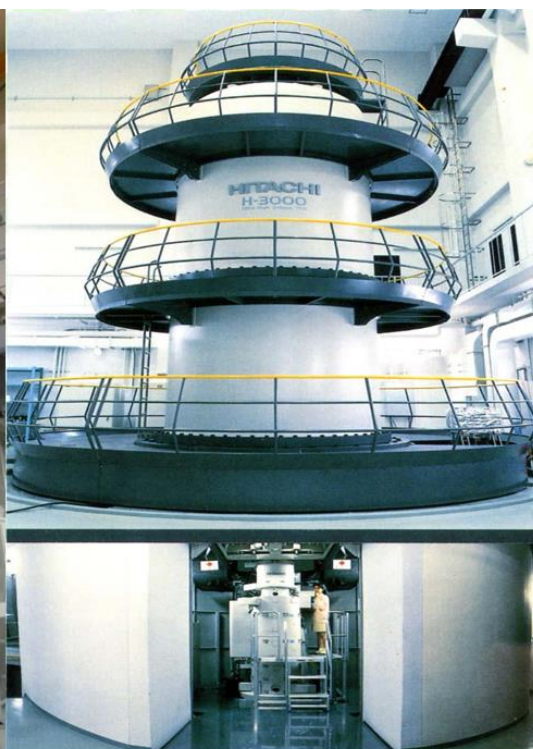
used in this study to characterize the dislocation loops in irradiated YSZ specimen; the details of the SADP used will be discussed in later sections. Two types of ultra-high voltage electron microscopes (Fig. 3.3), which belong to The Ultramicroscopy Research Center of Kyushu University and Research Center for Ultra-High Voltage Electron Microscopy Osaka University, were in use to perform in situ observation of radiation damage. Some characteristic features of those UHVEM is summarized in Table 3.1.

Table 3.1: Characteristic features of the UHVEMs used in this research work

Specification	H3000 UHVEM (Hitachi) Osaka University	JEM-1300NEF (JEOL) Kyushu University
High Voltage	3.0 MV	1.25 MV
Stability of high voltage	$< 2.0 \times 10^{-6} \text{ min}^{-1}$	$8 \times 10^{-7} \text{ min}^{-1}$
Cathode	LaB ₆ single crystal	LaB ₆ single crystal
Beam current	Maximum 20 μA	Maximum 15 μA
Lens Configuration	Six-step lens system No image rotation	Eight-step lens system No image rotation
Magnification	$\times 200$ to 1,000,000	$\times 200$ to 1,200,000
Resolution	0.14 nm	0.12 nm
Spherical aberration coefficient	$< 10 \text{ nm}$	2.2 mm
Chromatic aberration Coefficient	$< 10 \text{ nm}$	3.7 mm
Defocused point	Minimum 5 nm	Minimum 1 nm
Specimen Chamber Vacuum	$5 \times 10^{-6} \text{ Pa}$	$2 \times 10^{-6} \text{ Pa}$



JEM-1300NEF TEM (JEOL Ltd.)
Ultra-microscopy Research Center,
Kyushu University



Ultra-High Voltage Electron
Microscope (Hitachi H-3000)
Osaka University

Fig. 3.3: 1.25 and 3.0 MeV transmission electron microscopes in Kyushu and Osaka University respectively used for this research work.

3.3 SPECIMEN PREPARATION:

We know electrons are strongly scattered within a solid due to the large forces acting on an electron when it passes through the electrostatic field within each atom. It is, therefore, a TEM specimen must be thin enough to minimize the diverse of electron beam at the exit surface of the specimen to form an image with appropriate short exposure time. TEM specimen preparation involves ensuring that the thickness of at least some regions of the specimen are within the thickness range of 10 nm to 1 μm . Thus, depending on the materials involved, specimen preparation may occupy the bulk of the work involved in transmission electron microscopy [4]. Practical details of TEM specimen preparation technique are described elaborately in the text books [5, 6] with common sequence of preparation, such as: ultrasonic disk cutting, dimpling, and ion-milling [7]. The specimen used in this study is YSZ containing 8 mol% Y_2O_3 . The specimen preparation started from 8 mol% Y_2O_3 doped ZrO_2 powders supplied by Furuuchi Chemical Co. The details of 8 mol% YSZ specimen preparation will be described in chapter 4, section 4.2, but the general sequence of the technique is presented here as a flow-chart (Fig. 3.4).

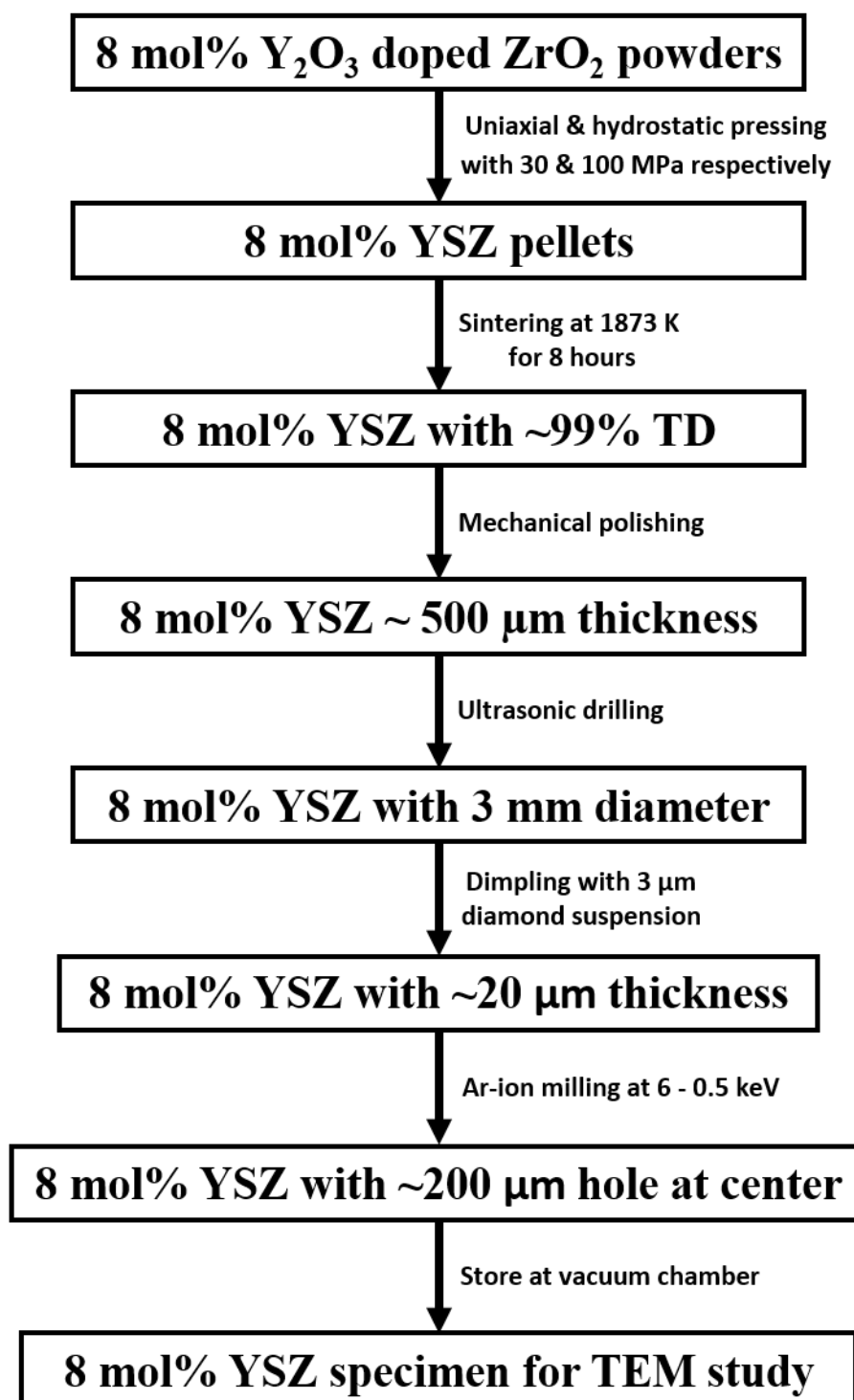


Fig. 3.4: Flow-chart showing the preparation sequence of 8 mol% YSZ specimen for TEM study. ‘TD’ stands for theoretical density.

3.4 IRRADIATION CONDITIONS AND DATA ACQUISITION:

3.4.1 *In situ* observation of defects in of 8 mol% pristine YSZ:

In situ observation of defect cluster formation and evolution of dislocation loops in pristine YSZ were performed at different irradiation temperatures from 300 to 773 K with a range of incident electron energies from 1.25 to 3.0 MeV. Irradiation experiments at 1.25 MeV electron energy were conducted by JEM-1300NEF (JEOL Ltd.) at The Ultra-microscopy Research Center of Kyushu University up to an electron fluence of $\sim 4.0 \times 10^{26} \text{ m}^{-2}$, and the experiments at 1.5, 2.0, 2.5 and 3.0 MeV electron energy were carried out with an ultra-high voltage electron microscope (H-3000, Hitachi Ltd.) at Research Center for Ultra High Voltage Electron Microscopy (UHVEM) of Osaka University up to an electron fluence of $\sim 2 \times 10^{27} \text{ m}^{-2}$. The electron irradiation was performed by using a focused electron beam with a size of around 1-1.5 μm in diameter, which is assumed to be close to a Gaussian distribution. The nucleation and growth process, discussed here, were recorded *in situ* by bright-field (BF) TEM technique either with a diffraction vector of $\mathbf{g} = 200$ or $1\bar{1}1$. YSZ specimen was irradiated at 3.0 MeV and irradiation temperature ranging from 873 to 973 K for approaching to a concluding decision. The details of the irradiation condition for pristine YSZ specimens are presented in the next page.

The $g \cdot b$ analysis of the dislocation loops at 3.0 MeV and 773 K was performed to characterize the type of the loops. Electron beams illuminated along the [110], [111] and [120] directions (Fig. 3.6) were used to check the visibility of the dislocation loops at different g vectors.

High Voltage (MeV)	1.25	1.5	2.0	2.5	3.0
Electron Flux (m ⁻² s ⁻¹) (Dose Rate (× 10 ⁻³ dpa/s))	1.3 × 10 ²⁴ (O: 1.7, Zr: 0.7)		-	2.0 × 10 ²⁴ (O: 1.5, Zr: 1.3)	
Temperature (K)	300		-		773
Irradiation Time (sec)	~ 1200				

Fig. 3.5: Irradiation conditions used to study dislocation evolution in pristine YSZ specimen.

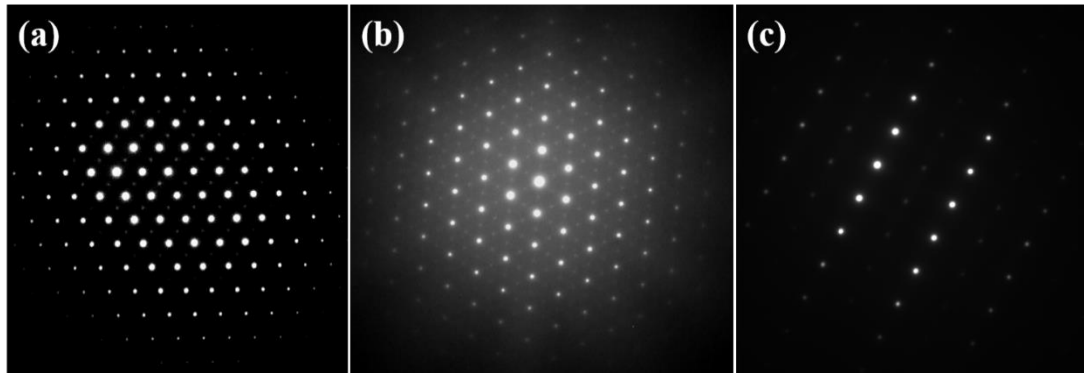


Fig. 3.6: Selected area diffraction (SAD) pattern under electron beam from [011] (a), [111] (b) and [120] (c) direction used for $g \cdot b$ analyses.

3.4.2 Beam size and flux intensity measurement:

The shape of the focused electron beam, used for *in situ* irradiation, was anticipated to be of a 2-dimensional Gaussian distribution [8]. Still the shape and intensity distribution of the beam was measured to identify the dependence of defect mobility on intensity distribution. The current was recorded with a Faraday cage in a systematic way at distinct position of the electron beam, and then the electron flux at that position was calculated. The details of findings with figurative explanation will be addressed in chapter 4.

3.4.3 *In situ* observation of defect evolution in ion-irradiated YSZ:

Similar to the *in situ* observation of defect evolution under electron irradiation in pristine YSZ, the defects in ion-irradiated YSZ was also studied under ambient and elevated irradiation temperatures. YSZ specimen of around 150 μm thickness was prepared at similar procedure described in section 3.3 and then, first subjected to $5 \times 10^{11} \text{ cm}^{-2}$ Xe ion irradiation at 300 K in Ion Accelerator Facility, JAEA. Ion-irradiated YSZ specimen were sent through dimpling and ion-milling (only in the un-irradiated side of the specimen) process to prepare wedge-shaped thin foil suitable for TEM.

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Chapter 4

Defects in 8 mol% Pristine YSZ at Different e^- Energies and Irradiation Temperatures

An experiment is a question which science poses to nature, and a measurement is the recording of nature's answer.

*-Max Planck
(1858 - 1947)*

4.1 INTRODUCTION:

Yttria stabilized cubic zirconia (YSZ) has been attracting great attention of researchers and subjected to theoretical and experimental research works for decades mainly due to its exceptional structural stability against adverse radiation environment. Previous ion-irradiation studies [1-10] have shown that YSZ cannot be amorphized in severe radiation environment, and it is, therefore, considered to be one of the potential matrices to use in extreme environments such as diluent of inert matrix fuels (IMF) and solid oxide fuel cells (SOFC) [11]. Moreover, along with CeO_2 [12, 13], as it is isostructural with UO_2 , ThO_2 , and PuO_2 , YSZ has also been used as a surrogate material for evaluating the performance of nuclear fuel and inert matrices in extremely high radiation environment [14, 15].

In practice YSZ, as a fuel matrix, should subsist in a high radiation exposure consisting of different types of radiation. Recent radiation damage studies on YSZ, both theoretically and experimentally, mainly worked with ion irradiation covering an

wide energy range of a few MeV [7, 16] to several GeV [17] and investigated point-defect creation, irradiation induced damage build-up, the interaction between implanted ions and radiation defects [18], and damage recovery [8] as well. Yasuda et al. have discussed microstructure evolution of YSZ through transmission electron microscopy (TEM) under irradiation with electrons and/or ions. They found anomalous formation of large defect clusters, which transformed into dislocation network after reaching a critical diameter of about 1.0-1.5 μm [19]. The formation of defect clusters were discussed to be dislocation loops consists of oxygen ions, which were formed due to the selective displacement of oxygen sublattice in YSZ.

In this chapter, a systematic series of experiments were performed to address the contribution of irradiation temperature and electron energy on the evolution of microstructure in YSZ. High voltage transmission electron microscopy (HVTEM) is used to investigate the evolution of dislocation loops in YSZ. The defect evolution mechanism and its dependence on electron energy and irradiation temperature are discussed based on the theoretical and experimental background described in chapter 2. Threshold displacement energy, the most important parameter affecting the defect formation behavior, is also bracketed for cation sublattices.

4.2 MATERIALS AND EXPERIMENTAL PROCEDURE:

Yttria-stabilized cubic zirconia (YSZ) pellets were prepared by compacting ZrO_2 containing 8 mol% Y_2O_3 powders supplied by Furuuchi Chemical Co. by uniaxial pressing using a pressure of 30 MPa and subsequent hydrostatic pressing in water (130 MPa) for densification. These green pellets were covered by YSZ powders with the same chemical composition to avoid direct contact between the pellets and an alumina ($\alpha\text{-Al}_2\text{O}_3$) melting pot during the sintering. Polycrystalline YSZ specimens were obtained by sintering the pellets in air at 1873 K for 8 hours. The density of sintered compacts were evaluated by Archimedes method (water immersion) [20] to be 99% theoretical density. A part of the sintered pellets were crashed into powders and were subjected to X-ray diffraction (XRD) measurement to be confirmed that produced YSZ pellets were consists of only fluorite structure. Disk specimens of 3.0 mm in diameter, prepared by mechanical shaping followed by ultrasonic drilling of sintered polycrystalline YSZ specimens, were subjected to Ar-ion milling processes at 6 keV to prepare wedge-shaped thin foils suitable for TEM. Finally, the specimens were subjected to ion-thinning gradually with lower energy ions to a final polishing energy of 0.5 keV, to minimize the Ar-ion damage.

In situ observation of defect cluster formation and evolution of dislocation loops were performed at different irradiation temperatures from 300 to 773 K with a

range of incident electron energies from 1.25 to 3.0 MeV. Irradiation experiments at 1.25 MeV electron energy were conducted by JEM-1300NEF (JEOL Ltd.) at The Ultra-microscopy Research Center of Kyushu University up to an electron fluence of $\sim 4.0 \times 10^{26} \text{ m}^{-2}$, and the experiments at 1.5, 2.0, 2.5 and 3.0 MeV electron energy were carried out with an ultra-high voltage electron microscope (H-3000, Hitachi Ltd.) at Research Center for Ultra High Voltage Electron Microscopy (UHVEM) of Osaka University up to an electron fluence of $\sim 2 \times 10^{27} \text{ m}^{-2}$. The electron irradiation was performed by using a focused electron beam with a size of around 1 μm in diameter, which is assumed to be close to a Gaussian distribution. The flux distribution of the focused electron beam will be shown in section 4.4.3, and the relationship between the beam intensity distribution and microstructure evolution will be discussed. The nucleation and growth process were recorded *in situ* by bright-field (BF) TEM technique either with a diffraction vector of $\mathbf{g} = 200$ or $1\bar{1}1$.

4.3 RESULTS:

Threshold displacement energy (E_d) is one of the major parameters for elucidating radiation damage in materials. As the values of E_d vary with sublattice of cations and anions, experimental measurements of E_d in ceramics are relatively difficult than pure metals [21, 22]. For this reason, reported values of E_d of O and Zr

sublattices in cubic zirconia are limited and vary within a certain range, thereby, it had been assumed that values E_d of O and Zr sublattices are in the range of 16-40 and 50-80 eV, respectively [22-24]. Fig. 4.1 shows calculated displacement cross-sections in YSZ through elastic collision process using McKinley-Feshback formula [25] against required incident energy. It is shown in Fig.4.1 that only oxygen sublattice is displaced selectively in YSZ at energies less than around 1.0 MeV because of the difference in mass and in E_d between Zr-cation and O-anion, and the displacement cross section for Zr ions start to increase at energies higher than around 1.5 MeV. It is, therefore, noted

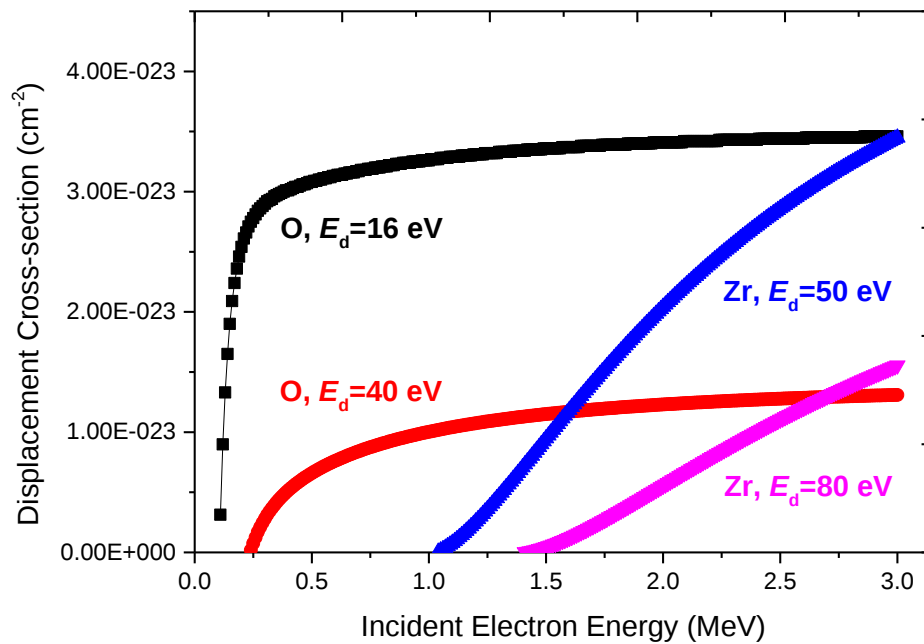


Fig. 4.1: Simulation results of elastic displacement cross-section for Zr and O ions as a function of incident electron energy. Displacement cross-section is plotted with threshold displacement energies of 16-40 eV for O sublattice and 50-80 eV for Zr sublattice.

that electron irradiation in YSZ changes the point defect formation condition with increasing energy from selective displacement damage on O-ion to the one both O-ion and Zr-cation displacement damage. The qualitative features of the defects at different irradiation energy are discussed sequentially in the following. The ratio of displacement damage in O ions/ cations as a function of increasing energy within the energy range used in the present study is also elaborately contended later on.

4.3.1 Irradiation with 1.25 MeV Electrons:

8 mol% yttria doped zirconia (YSZ) specimens were irradiated with 1.25 MeV electrons starting from 300 K. The irradiation temperature increased stepwise to 673 K to evaluate the type and mechanism of defects at different irradiation conditions. Fig. 4.2 (a) and (b) show BF-TEM images of YSZ specimens irradiated at 300 and 673 K, respectively with 1.25 MeV electrons to an identical fluence of $4.5 \times 10^{26} \text{ m}^{-2}$. In these BF images (Fig. 4.2 (a) and (b)), no defect clusters are seen to be nucleated under these irradiation conditions. Similarly, at intermediate temperatures of 373 and 573 K, defect clusters were not formed (image is not included here) under 1.25 MeV electron irradiation to a fluence of around $5 \times 10^{26} \text{ m}^{-2}$. It is anticipated from Fig. 4.1 that O ions are displaced at energies higher than around 0.25 MeV, while no or very few Zr ions are probably to be displaced under 1.25 MeV electron irradiation: the

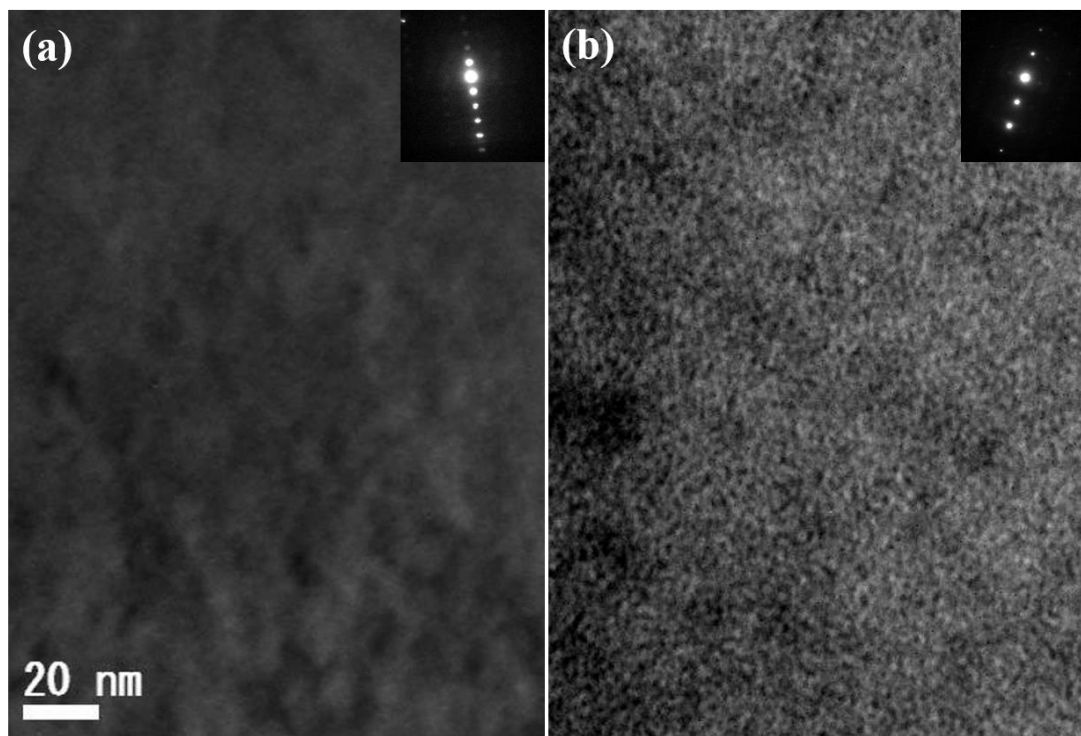


Fig. 4.2: Bright-field TEM images showing no defect clusters up to $4.5 \times 10^{26} \text{ m}^{-2}$ of electron fluence at 300 K (a) and 673 K (b) under 1.25 MeV e^- irradiation. Inset in (a) and (b) show the selected area diffraction pattern of the irradiation conditions.

estimated values of dpa for O and Zr ions are 3 and nearly 0, respectively under an assumption of E_d values ($E_{d,O} = 40$ eV, $E_{d,Zr} = 80$ eV). The oxygen point defects created by 1.25 MeV electron irradiation were, therefore, considered to be diminished by the recombination with empty interstitial sites in oxygen sublattice that were induced by the doping of trivalent Y^{3+} ions to compensate the charge neutrality [26-28]. On the other hand, it has been shown by Yasuda et al. [19] that 200 keV electron irradiation induces large anomalous defects in YSZ, which is considered to be consist of oxygen interstitials. The reason for the discrepancy to the microstructure shown in Fig. 4.2 and in ref. 19 is attributed to the prior irradiation with 300 keV O ions at 470 K. Note that 300 keV O-ion induce elastic displacement damage in both oxygen and cation sublattices. Defects induced by the prior irradiation of 300 keV O ions are considered to act as the nucleation sites [19, 29] of oxygen-type defects and become preferable for evolution of oxygen type defects at secondary radiations.

4.3.2 Irradiation with 2.0 MeV Electrons:

Fig. 4.3 displays *in situ* sequential TEM images in YSZ poly-crystals irradiated by a focused electron beam at 300 K with 2.0 MeV energy. The BF TEM images were shot at a diffraction condition of $g = 200$ and the electron beam direction was close to [012]. No defect clusters or dislocation loops were observed in the

specimen before the electron irradiation (Fig. 4.3 (a)), indicating that no obvious polishing damage was induced by Ar-ion milling. Tiny black dot-contrasts with a size of a few nm were started to be nucleated at the center of the focused electron beam at a fluence of around $3.5 \times 10^{26} \text{ m}^{-2}$ (an example is indicated in Fig. 4.3 (b) by an arrow), which were increasing in number and the size with higher fluence. At an electron fluence of $2.1 \times 10^{27} \text{ m}^{-2}$ (Fig. 4.3(d)), black dot contrasts and tiny dislocation loops, which were formed by growth of dot contrasts, were seen covering the whole irradiation beam area. The corresponding displacement damage for Zr and O ions is evaluated to be 1.9 and 3.8 dpa, with an assumption of E_d of 80 and 40 eV for Zr and O ions, respectively. It is also interesting to note that a large dislocation loop with around 200 nm in diameter was nucleated accompanying strong strain contrast at the periphery of the focused electron beam area (shown by a white arrow in Fig. 4.3(d)). This large loop is considered to be oxygen-type interstitial dislocation loop, since the size and contrast is analogous to the oxygen-type dislocation loops formed under electron irradiation [19].

According to the calculation of displacement cross-sections (Fig. 4.1), 2.0 MeV electron irradiation induces elastic displacement damage on both the Zr and O sublattices. Judged from the displacement condition for both oxygens and cations, and

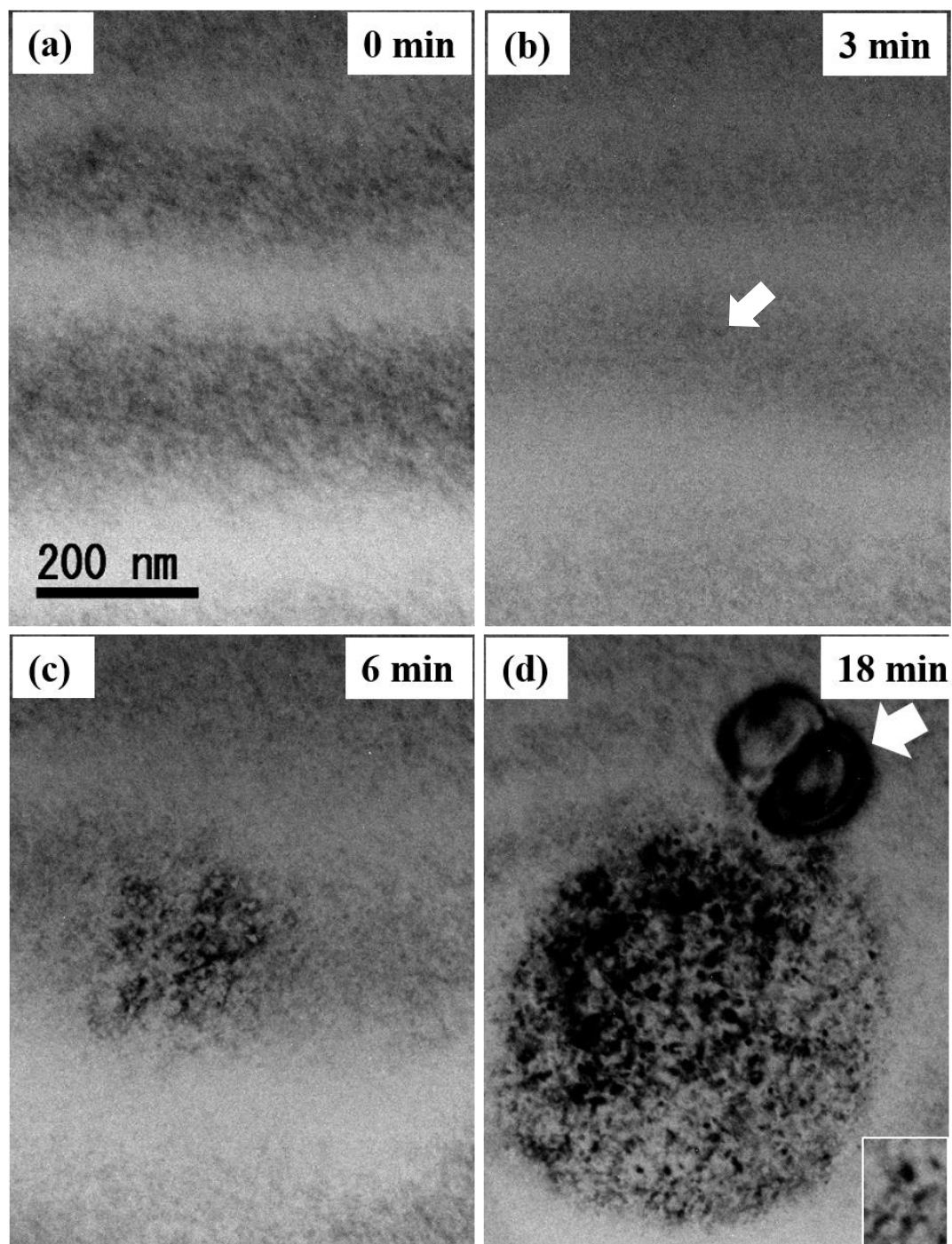


Fig. 4.3: Sequential *in situ* BF-TEM images showing the nucleation and growth of defects in YSZ poly-crystals irradiated with 2.0 MeV incident electron at 300 K at various dose levels: (a) un-irradiated, (b) $3.6 \times 10^{26} \text{ m}^{-2}$ (c) $7.0 \times 10^{26} \text{ m}^{-2}$, (d) $2.1 \times 10^{27} \text{ m}^{-2}$. The observations were performed from the [012] direction with $g = 200$ reflection. Inserted micrograph in (d) is a magnified image of the defects formed in (d). The white arrow in (d) points to an oxygen displacement type dislocation loop.

the difference in the size and contrast from oxygen-type dislocation loops (Fig. 4.3(d) and ref. [19]), the black dot-contrasts appeared in Fig. 4.3 (b)-(d) are presumably perfect dislocation loops consist of both O-anions and Zr-cations. As shown in chapter 2 (Table 2.2), the migration energies of oxygen vacancies and interstitials are much lower than those of zirconium ions, and the amount of displaced ions is larger for oxygen point defects than cation ones. It is, therefore, considered that excess oxygen interstitials migrate from the center towards the periphery of the focused electron beam, which is driven by the concentration gradient of displaced oxygen ions following the distribution of electron beam flux. Hence the large loop with oxygen-type was formed at the periphery of the irradiated beam (Fig. 4.3(d)). This will be discussed in the later section of 4.3.3. Along with these tiny perfect type dislocation loops, a numerous number of other defect clusters, which do not possess a distinguishable image but looks like diffuse dots [30], were also formed.

To understand the effect of irradiation temperature on the nucleation-and-growth process of dislocation loops and microstructure evolution, YSZ specimens were irradiated at elevated temperatures of 573, 673 and 773 K with 2.0 MeV electrons up to around the same electron fluence ($2.1 \times 10^{27} \text{ m}^{-2}$). In the cases of 573 K (Fig. 4.4) and 673 K (Fig. 4.5), large loops with strong strain contrast (indicated as white arrows in fig. 4.4 (b), (c) and 4.5 (c)), similar to the one shown in Fig. 4.3(d),

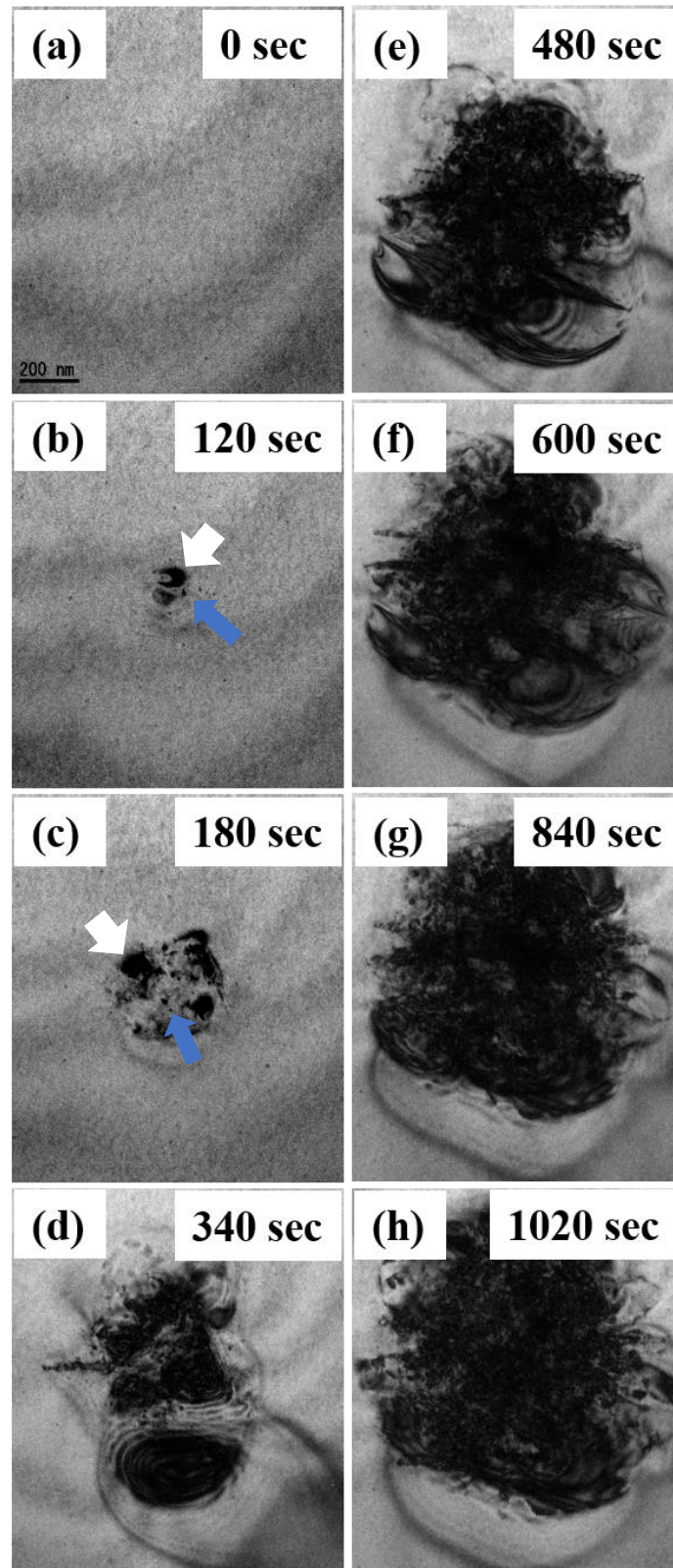


Fig. 4.4: Sequential *in situ* BF-TEM images showing the nucleation and growth of defects in YSZ poly-crystals irradiated with 2.0 MeV incident electron at 573 K at various dose levels up to $2.0 \times 10^{27} \text{ m}^{-2}$. The observations were performed from the [011] direction with $g = 1\bar{1}1$ reflection. The dot contrasts at the un-irradiated and irradiated matrices were examined to be contaminations evolved during ion-milling process.

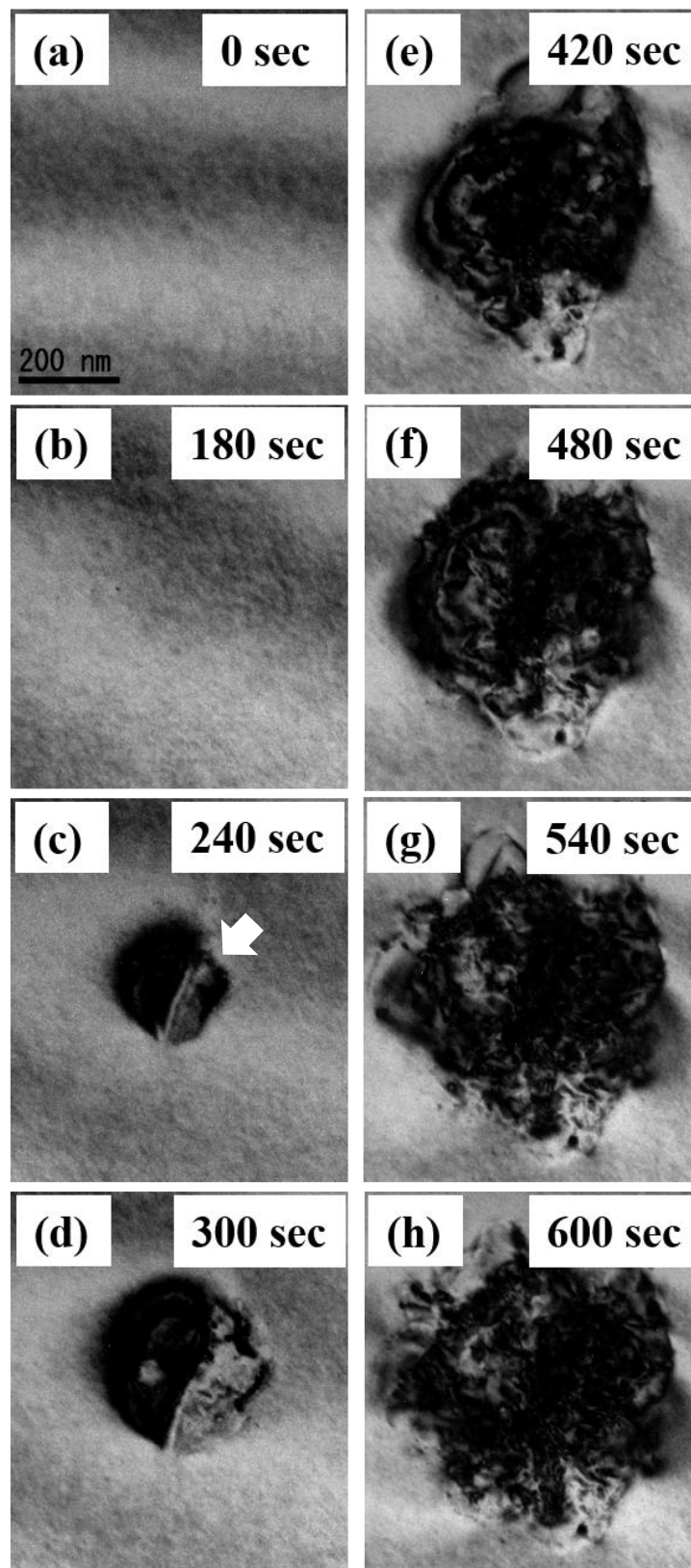


Fig. 4.5: Sequential *in situ* BF-TEM images showing the nucleation and growth of defects in YSZ poly-crystals irradiated with 2.0 MeV incident electron at 673 K at various dose levels up to $1.0 \times 10^{27} \text{ m}^{-2}$. The observations were performed from the [012] direction with $g = 200$ reflection.

were formed at the center of the irradiated area from the beginning stage of electron irradiation together with dot contrast of small defect clusters (indicated as blue arrow in fig. 4.4 (b), (c)), which increased the size and density with increasing electron fluence. Due to the strong strain contrast of large oxygen-type dislocation loops at the central part of the irradiated area, the small dot contrasts could not be clearly distinguished by *in situ* TEM experiments. As reported in ref. [19], the large dislocation loops grew very rapidly under electron irradiation and suddenly changed their contrast to dislocation lines. Fig. 4.6 presents a sequential change of the formation of oxygen-type dislocation loops, taken by video recording system under 2.0 MeV electron irradiation, showing that the conversion of oxygen-type dislocation loops to dislocation lines were observed repeatedly during the electron irradiation.

Rutherford backscattering spectrometry/channeling (RBS/C) experiments on ion irradiated zirconia [31] and pyrochlores [32] have shown that damage accumulation process consists of several distinct steps and it has been successfully fitted by multi-step damage accumulation (MSDA) model [33]. Debelle *et al.* [23] showed that 4 MeV Au^{2+} ions induce dislocation loops in YSZ, and that there is a significant variation of the threshold fluence for initiating the damage step depending on the irradiation temperature. The transition fluence from step 1 to step 2, which is the fluence where the accumulated damage in RBS/C experiments revealed a steep

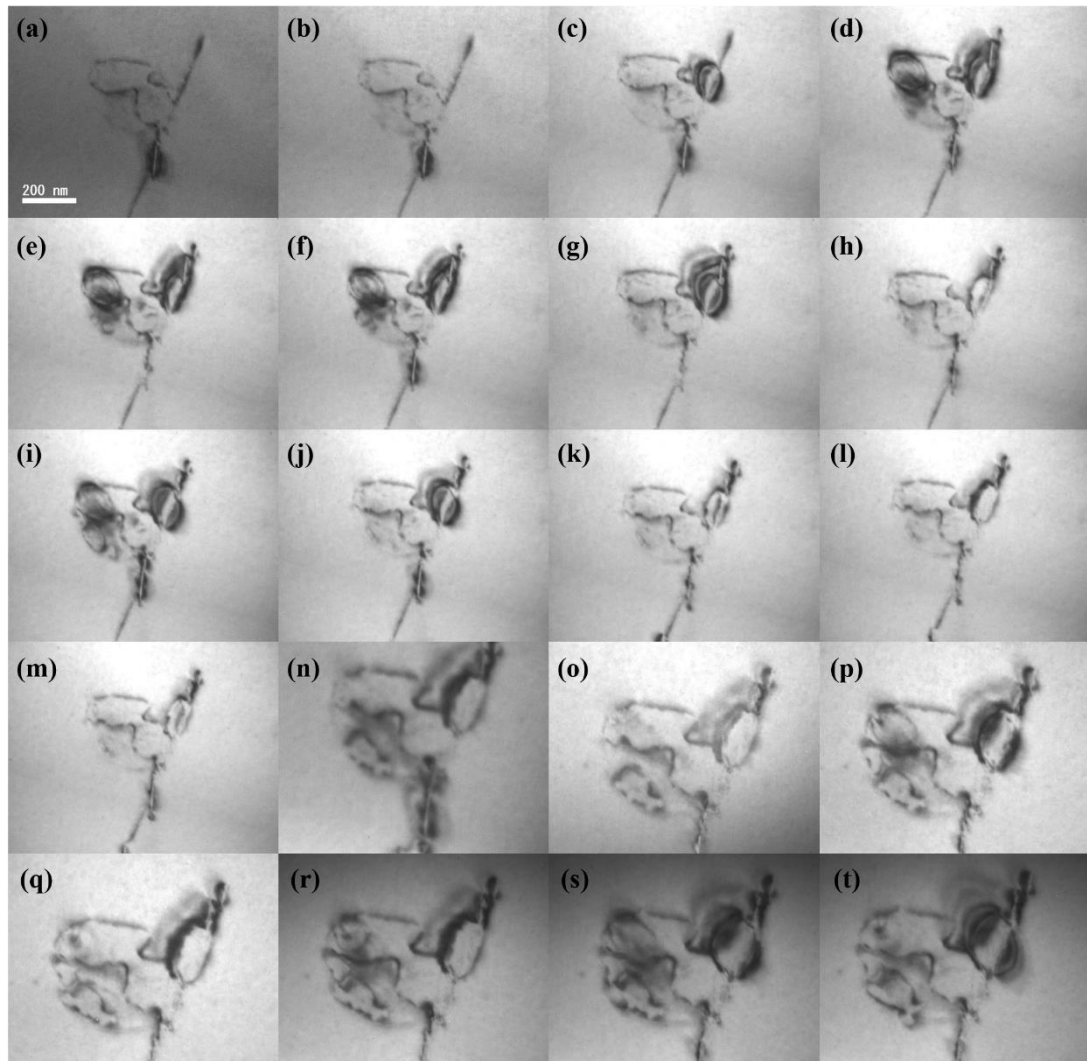


Fig. 4.6: Sequential images (taken at about 10 sec interval) showing the repeating nucleation, growth and conversion of oxygen type dislocation loops to dislocation lines in YSZ poly-crystals irradiated with 2.0 MeV focused electron beam at 723 K with a flux of $1.0 \times 10^{23} \text{ m}^{-2} \text{ s}^{-1}$. The observations were performed from the [110] direction with $g = 200$

increase, decreased with increasing irradiation temperature [23]. This suggests that the lattice disordering proceed relatively at lower fluence at higher temperature irradiation. Electron irradiation with 2.0 MeV at higher temperature attributes the higher mobility of displaced Zr and O ions, and results in the formation of small perfect dislocation loops in the central part of the focused electron beam. Those defects induce stronger stress and strain field around the loops compared to irradiation at relatively low temperature of 300 K, and thereby the perfect loops worked as nucleation sites for oxygen interstitial-type dislocation loops from the beginning of the irradiation. As, is discussed in chapter 2, that the displaced interstitials and vacancies in a thinner part of specimens preferably migrate to the surface sinks [34], so thicker part of the specimen had been chosen for irradiation at 573 and 673 K with 2.0 MeV electron irradiation to avoid annihilation of point defects, especially oxygen point defects at surface sinks.

At irradiation of 773 K with 2.0 MeV electrons, however, microstructure evolution in YSZ was entirely different from those observed at 300, 573 and 673 K. Fig. 4. 7 shows sequential *in situ* BF TEM image irradiated with 2 MeV at 773 K up to a fluence of $1.3 \times 10^{27} \text{ m}^{-2}$, at which only dislocation loop contrast, which is considered to be perfect dislocation loops, were formed. The loops have larger size than the dot-contrast formed at lower temperatures, and the density was lower.

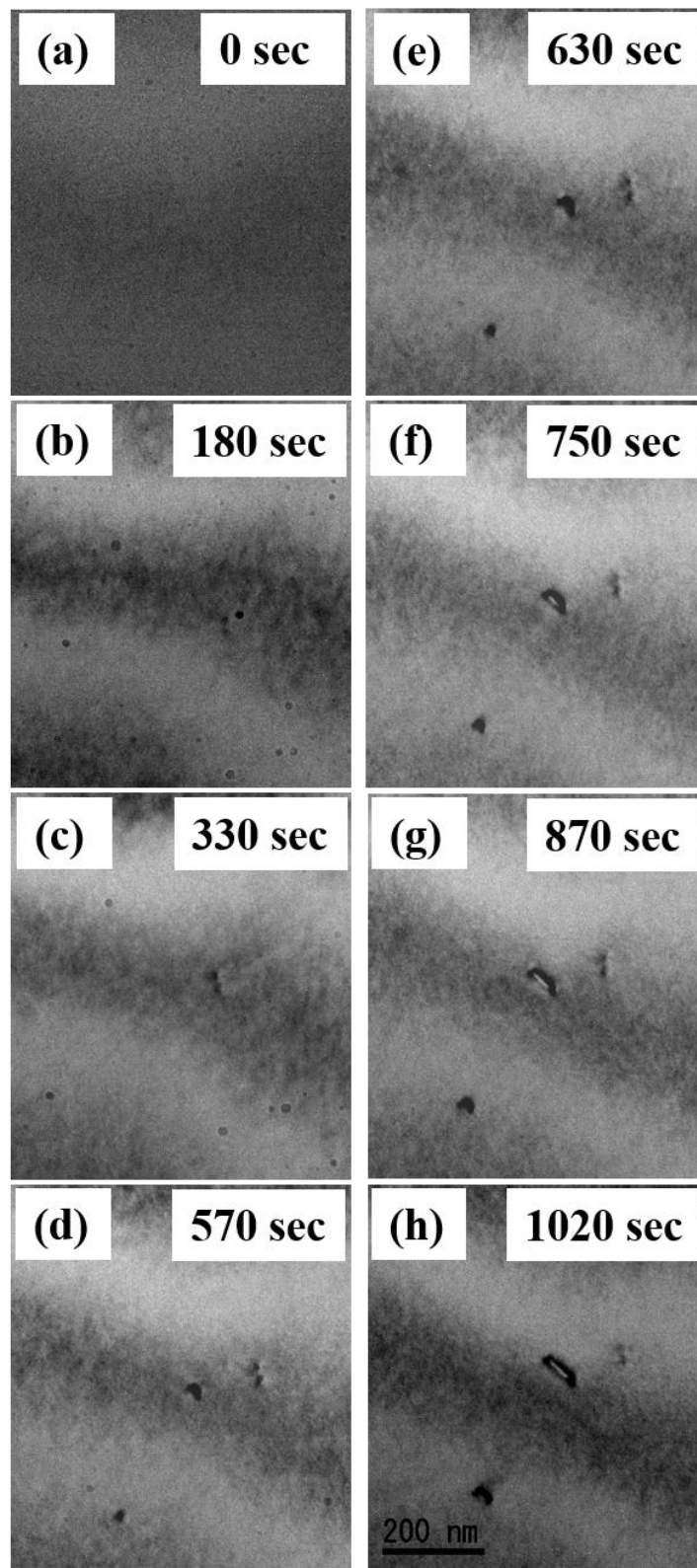


Fig. 4.7: Sequential BF-TEM image showing the defects nucleated in YSZ poly-crystals irradiated with 2.0 MeV incident electron at 773 K up to $1.3 \times 10^{27} \text{ m}^{-2}$. The observations were performed from the [011] direction with $\mathbf{g} = \bar{1}\bar{1}1$ reflection. The dot contrasts at the un-irradiated and irradiated matrices were examined to be contaminations evolved during ion-milling process.

Oxygen-type large dislocation loops were not formed at this irradiation temperature. Namely, only one type of defects (perfect dislocation loops) were formed at 773 K, in contrast to microstructure evolution at lower temperatures. Increasing temperature should induce enhanced defect clustering and formation of larger defect clusters as reported in 4 MeV Au²⁺ ion irradiated cubic yttria-stabilized zirconia single crystals [16]. At this irradiation condition (Fig. 4.7) huge number of recombination of oxygen point defects is most likely to occur along with surface sink effect during high temperature, due to the higher mobility of interstitials and vacancies of O ions, [35], resulting no formation of the oxygen-type dislocation loops and a low density of perfect type dislocation loops.

4.3.3 Irradiation with 3.0 MeV Electrons:

Fig. 4.8 shows the sequential *in situ* BF TEM images of the defects nucleated in YSZ specimen with 3.0 MeV electron irradiation at 773 K. At this elevated temperature and high electron energy irradiation, perfect-type of dislocation loops were started to nucleate from the very beginning of irradiation and increased in size and number with higher fluences. Higher density of perfect dislocation loops with 3.0 MeV electron irradiation than 2.0 MeV suggests an important role of the ratio of displacement damage on cation and oxygen sublattice for the nucleation of perfect

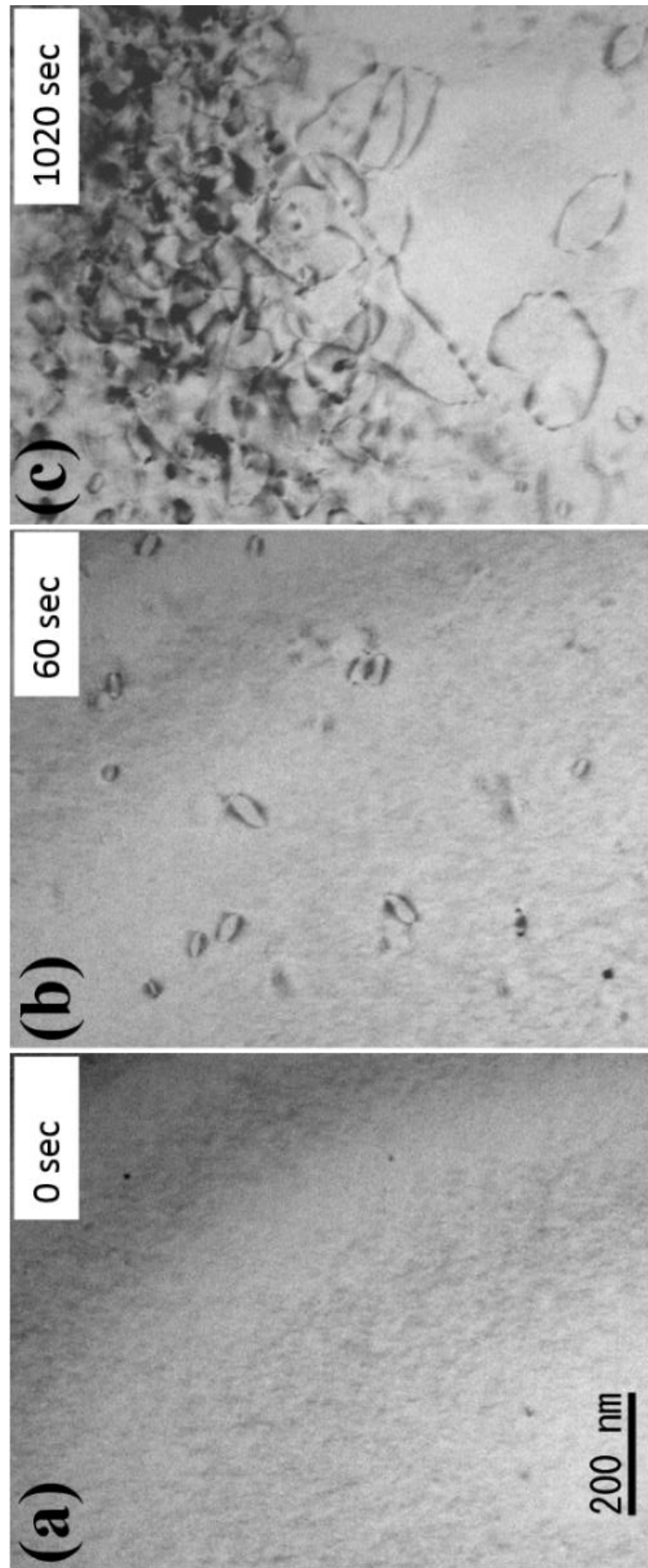


Fig. 4.8: Sequential *in situ* BF-TEM images showing the nucleation and growth of defects in YSZ poly-crystals irradiated with 3.0 MeV incident electron at 773 K at various dose levels: (a) un-irradiated, (b) $7.8 \times 10^{25} \text{ m}^{-2}$, and (c) $1.3 \times 10^{27} \text{ m}^{-2}$. The observations were performed from the $[112]$ direction with $g = 1\bar{1}1$ reflection. The dot contrasts at the unirradiated and irradiated matrices were examined to be contaminations evolved during ion-milling process.

dislocation loops, although further investigation is necessary to proceed the discussion. Similar to the microstructure change with 2.0 MeV at 773K, no large oxygen-type dislocation loops were nucleated at this irradiation condition. Mobility of Zr and O ions were increased with increasing irradiation temperature, and at the temperature of 773 K is considered to reach the critical temperature at which only perfect type dislocation loops were nucleated and grown. It is also noted that higher density of perfect dislocation loops are formed with 3.0 MeV electron irradiation than 2.0 MeV. This suggests an important role of the ratio of displacement damage on cation and oxygen sublattice for the nucleation of perfect dislocation loops (this will be discussed in later section 4.4.3).

Fig 4.9 shows the defects nucleated in YSZ under 3.0 MeV electron irradiation at 300, 573 and 673 K with almost an identical electron fluence ($1.1 \times 10^{27} \text{ m}^{-2}$). At temperatures of 300 and 573 K (Fig. 4.9 (a) and (b)), high density of tiny dot contrast is preferentially formed at the center part of the focused electron beam, as well as the formation of oxygen type dislocation loops. At 673 K, lower density of perfect and oxygen displacement type dislocation loops found existing contemporarily supporting the assumption: mobility of the constituent atomic species and vacancies, as described earlier, is an important factor for nucleation of dislocation loops.

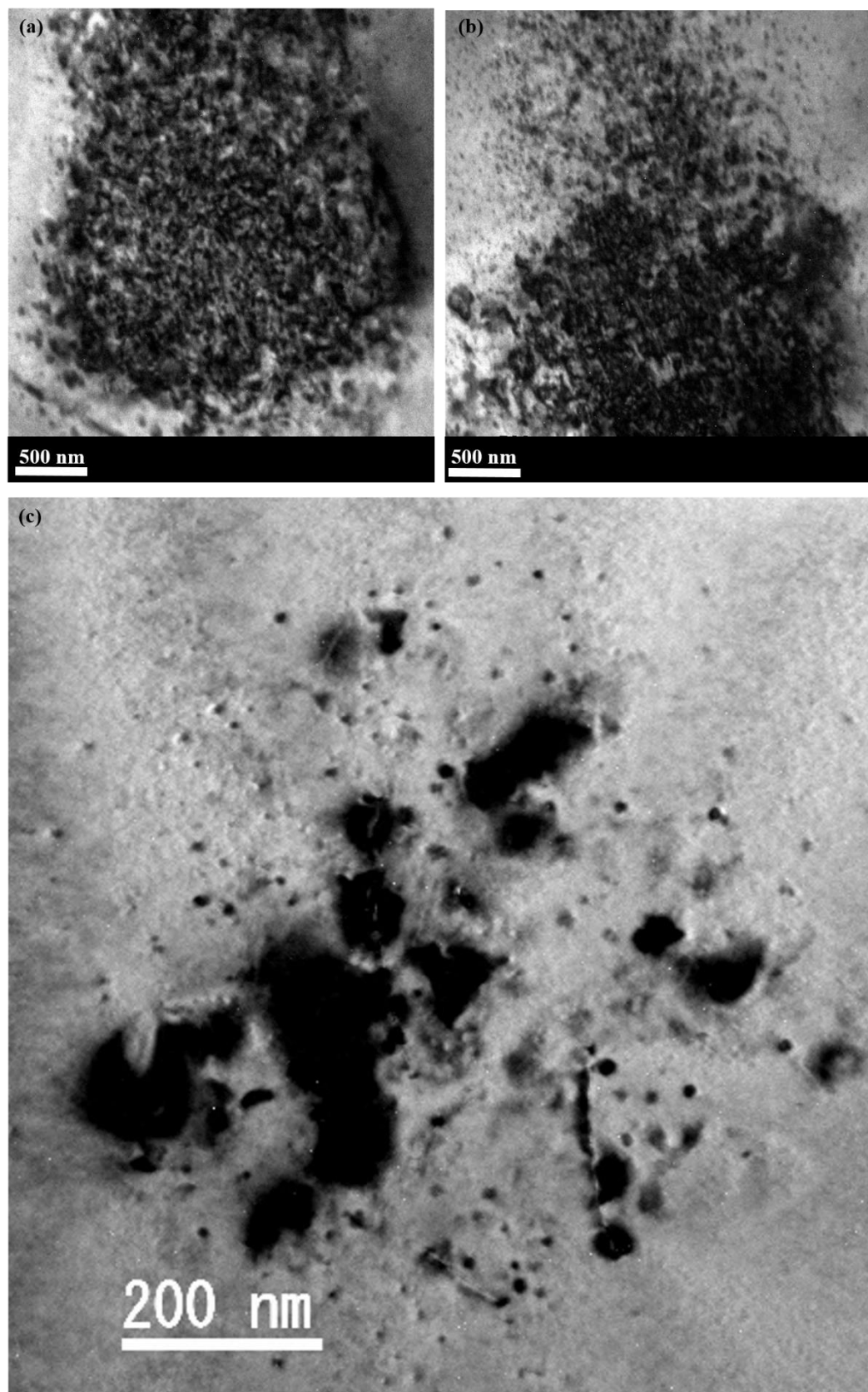


Fig. 4.9: Bright-field TEM images showing defect clusters under 3.0 MeV electron irradiation at 300 (a), 573 (b) and 673 K (c) with about $1.1 \times 10^{27} \text{ m}^{-2}$ of electron fluence in each case.

4.3.4 Irradiation with 1.5 MeV Electrons:

As described in 4.3.2 and 4.3.3, microstructure evolution in YSZ depend strongly on electron energy and irradiation temperature. Two types of extended defects, that is oxygen type dislocation loops and perfect dislocation loops, are formed. In the following two sections, microstructure evolution at intermediate electron energy irradiation (1.5 and 2.5 MeV) and different irradiation temperatures will be shown to further discuss the kinetic behavior of defects in YSZ.

A series of experiments were performed at 1.5 MeV electron irradiation with irradiation temperature ranging from 300 to 573 K. The sequential TEM images of the defects nucleated in YSZ are included in the following pages (Fig. 4.10 - 4.14). The information on the beam directions and diffraction conditions are described in the image captions. Different from the results obtained with 1.25 MeV electrons, radiation-induced defects were observed with 1.5 MeV at all irradiation conditions.

Fig. 4.10 shows that large loops were started to nucleate at 300 K from the beginning of the experiment at $8.5 \times 10^{22} \text{ m}^{-2} \text{ s}^{-1}$ electron flux, which were increased in size and density with increasing fluence. Only larger sized oxygen-type dislocation loops were formed and dot contrast as seen in Fig. 4.3 (perfect dislocation loops) were hardly observed. This is significantly different from the microstructure evolution with 2.0 MeV electron irradiation at same irradiation temperature (Fig. 4.3). As

discussed in section 4.1, a calculation of the displaced cross-section predicts that both O and cation sublattices are displaced with 1.5 MeV electrons. However, due to the large difference in mass between cations and anions, the number of displaced cations is significantly less than oxygen ions. It is also recalled that no defect clusters are formed with 1.25 MeV electron irradiation in YSZ although there should be displacement damage in oxygen sublattice. The formation of oxygen-type dislocation loops with 1.5 MeV electron irradiation is, therefore, an indication that there exists displacement damage in cation sublattice. Oxygen-type dislocation loops are considered to be nucleated at sites where point defects and/or small defect clusters including cation point defects exists.

Similar defect evolution trend of defect nucleation and clustering were observed at 323 and 373 K with a slower growth rate, compared to the case at 300 K (Fig. 4.11 and 4.12). At elevated irradiation temperature of 573 K, small dot contrasts started to nucleate at around $1.3 \times 10^{27} \text{ m}^{-2}$ electron fluence and later on at around $2.0 \times 10^{27} \text{ m}^{-2}$ only perfect stoichiometric dislocation loops were formed as shown in Fig. 4.13. Very high electron fluence of $6.2 \times 10^{27} \text{ m}^{-2}$ with further higher temperature (773 K) caused higher mobility of O and cation sublattices leading to higher recombination of vacancy and interstitials and only perfect type of dislocation loops were observed (Fig. 4.14).

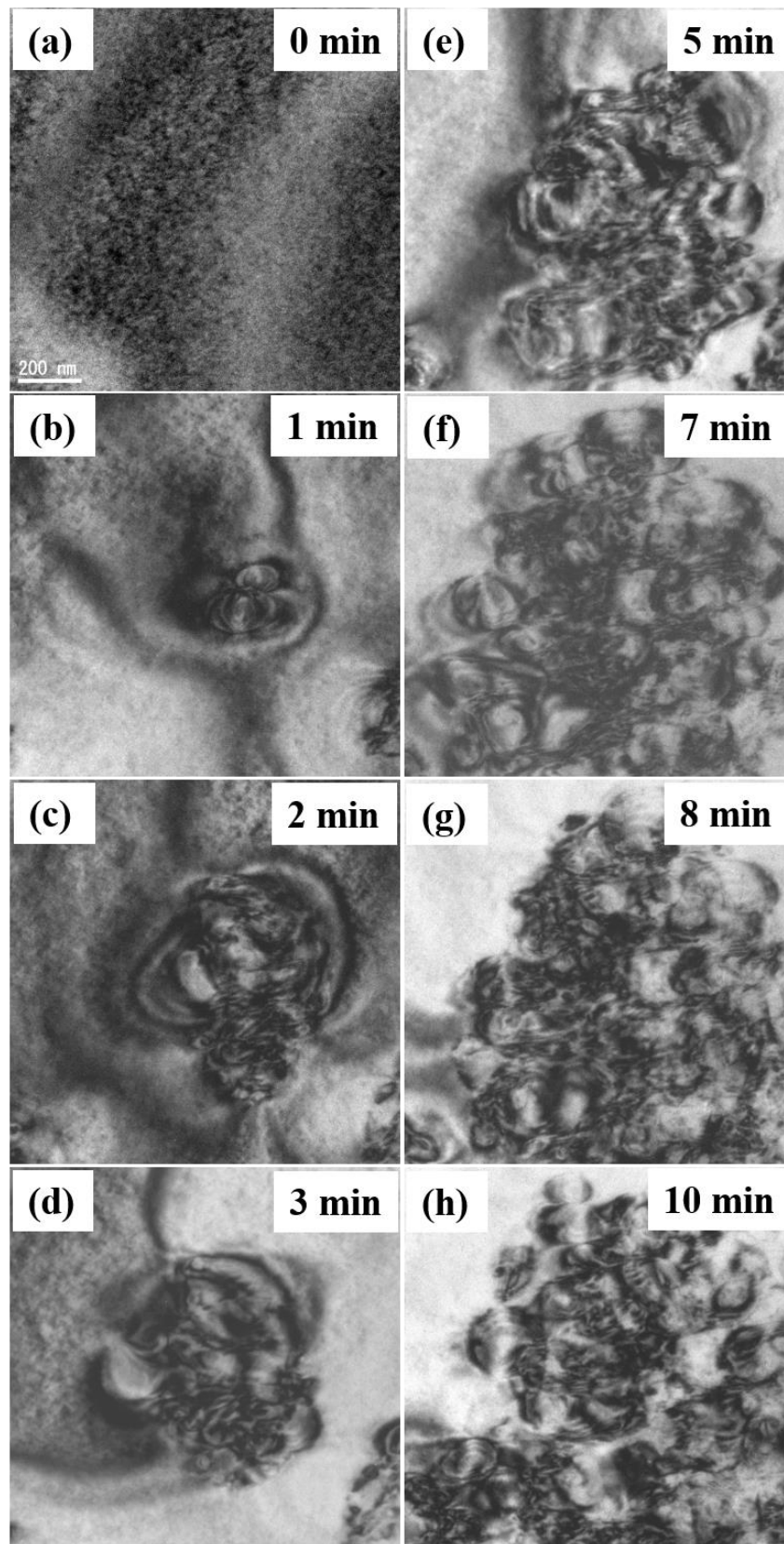


Fig. 4.10: Bright-field TEM images showing defect clusters up to $5.1 \times 10^{25} \text{ m}^{-2}$ of electron fluence at 300 K under 1.5 MeV e^- irradiation. The observations were performed from the [001] direction with $g = 200$ reflection.

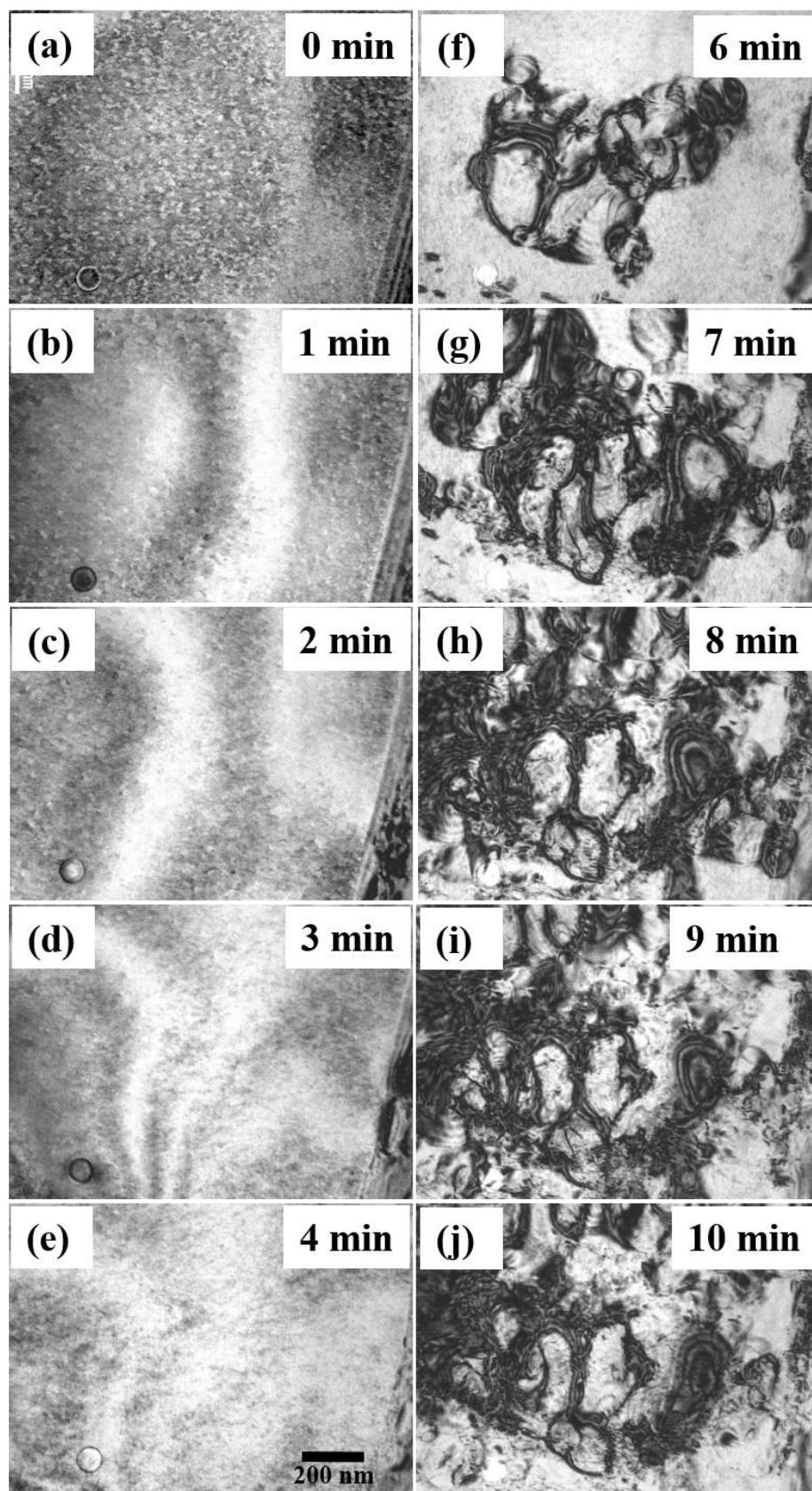


Fig. 4.11: Bright-field TEM images showing defect clusters up to $1.3 \times 10^{27} \text{ m}^{-2}$ of electron fluence at 323 K under 1.5 MeV e^- irradiation. The observations were performed from the [110] direction with $g = 111$ reflection.

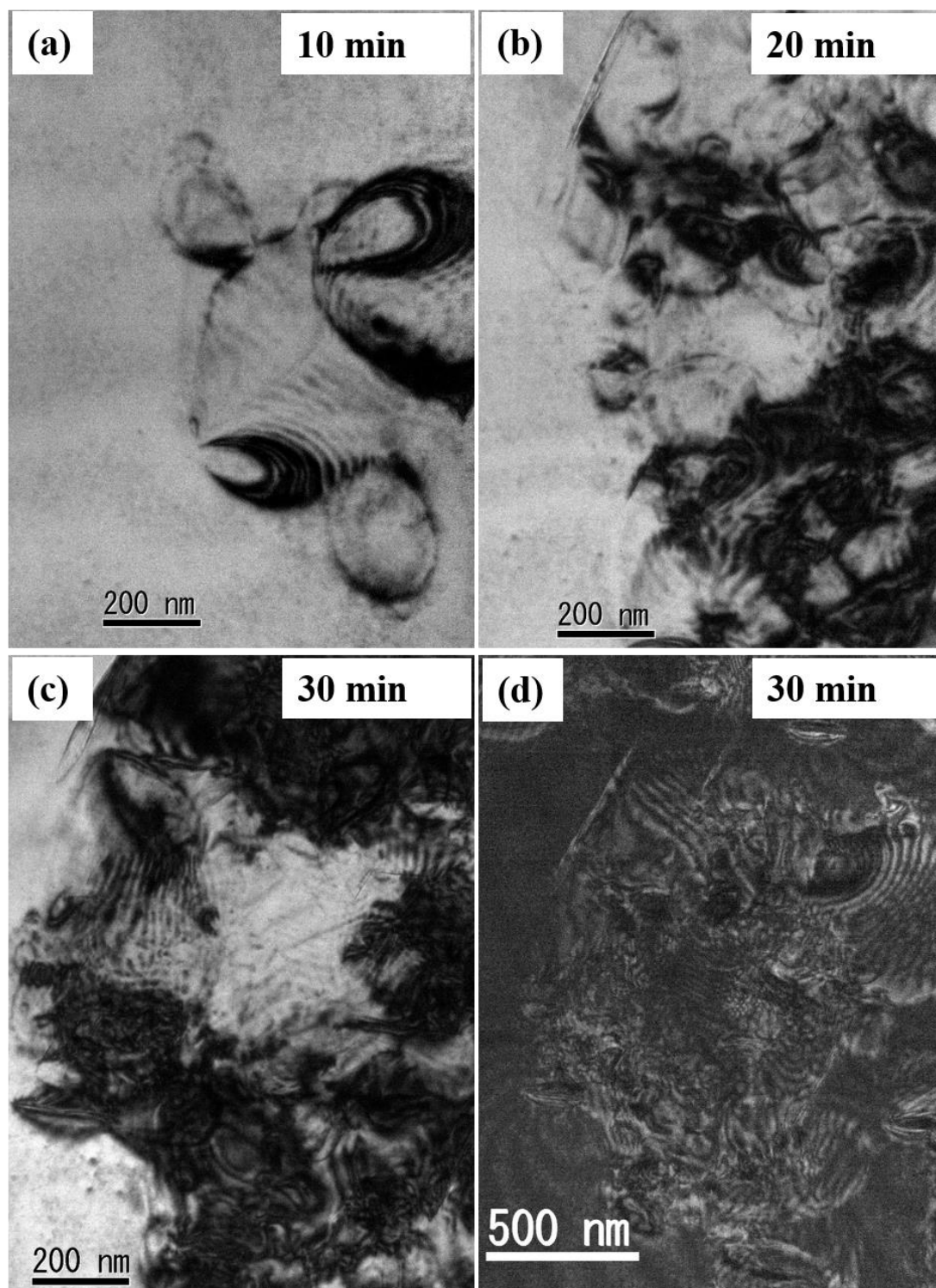


Fig. 4.12: *in situ* BF-TEM images (a), (b), (c) and DF-TEM image (d) showing the nucleation of defects in YSZ poly-crystals irradiated with 1.5 MeV incident electron at 373 K at various dose levels: (a) $6.6 \times 10^{26} \text{ m}^{-2}$, (b) 1.3×10^{27} and (c) & (d) $1.9 \times 10^{27} \text{ m}^{-2}$. The observations were performed from the [110] direction with $g = 111$ reflection.

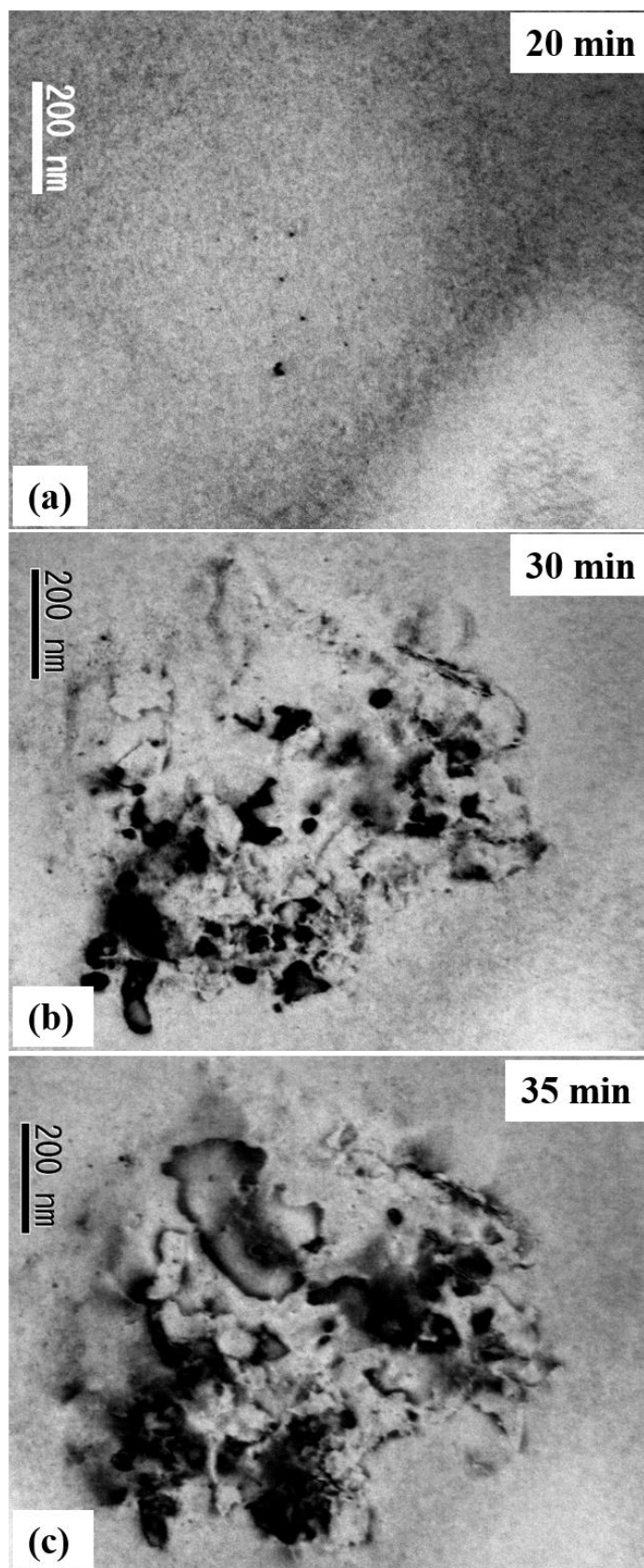


Fig. 4.13: Sequential *in situ* BF-TEM images showing the nucleation and growth of defects in YSZ poly-crystals irradiated with 1.5 MeV incident electron at 573 K at various dose levels: (a) $1.3 \times 10^{27} \text{ m}^{-2}$, (b) $2.0 \times 10^{27} \text{ m}^{-2}$, and (c) $2.3 \times 10^{27} \text{ m}^{-2}$. The

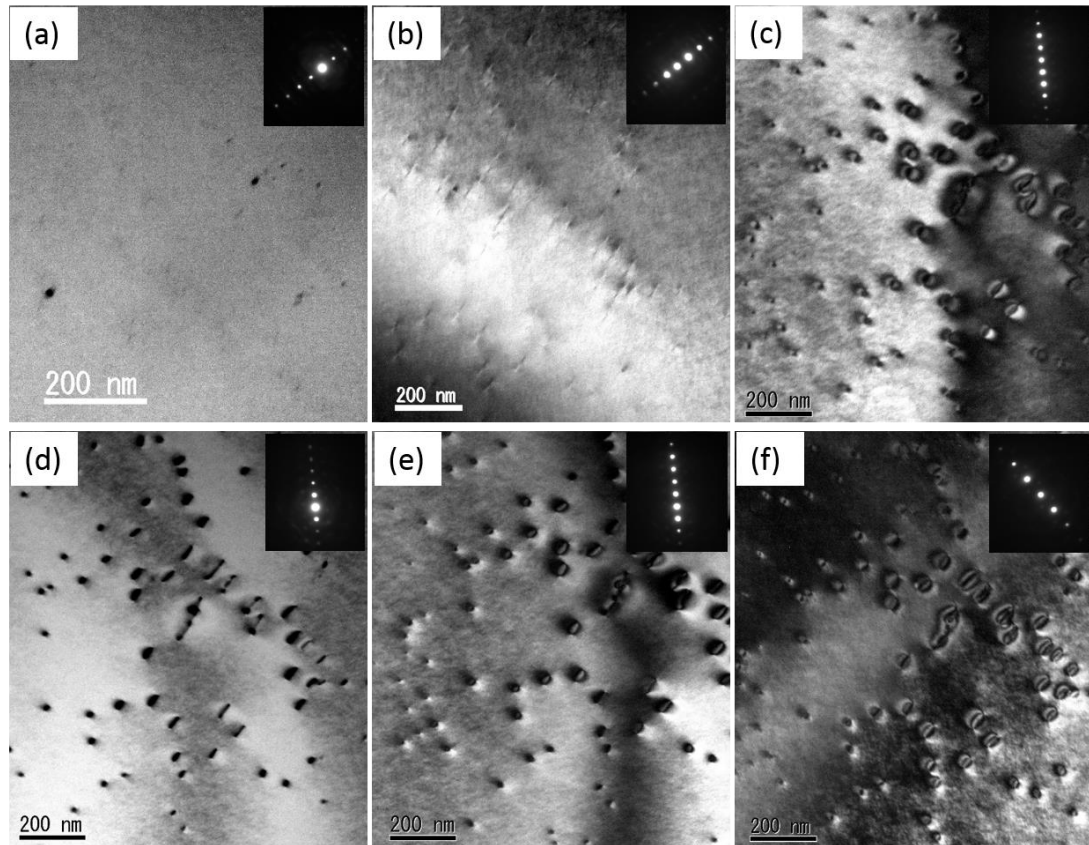


Fig. 4.14: *In situ* bright-field TEM images showing the defects in YSZ poly-crystals irradiated with 1.5 MeV incident electron at 773 K and $6.2 \times 10^{27} \text{ m}^{-2}$ electron dose. The irradiation was performed from the [011] direction and the observation was done with different $\mathbf{g}$ as shown in-set in each images.

4.3.5 Irradiation with 2.5 MeV Electrons:

Figs 4.15 and 4.16 show sequential changes of BF TEM images irradiated with 2.5 MeV electrons at temperatures 300 and 573 K, respectively. At 300 K, tiny perfect loops were initially nucleated at the central part of the specimen (Fig. 4.15 (b) and (c)), and at around a fluence of $1 \times 10^{27} \text{ m}^{-2}$ several oxygen-type dislocation loops were formed at the periphery of the focused electron beam (Fig. 4.15 (d)). Tiny perfect loops increased their number to cover the whole electron beam to be around 800 nm in diameter at $1.5 \times 10^{27} \text{ m}^{-2}$ (Fig. 4.15 (i)). The sequential change in microstructure shows similar characteristic features as observed under 2.0 MeV electron irradiation, (as shown in Figs. 4.15 and 4.16). At higher temperature of 573 K, both oxygen-type and perfect dislocation loops were formed preferentially at the center part of the focused electron beam. This is also analogous to the microstructure change observed with 2.0 MeV. Overall microstructure evolution showed the same tendency between 2.0 and 2.5 MeV. As higher irradiation energy induces larger amount of displacement damage, a higher number of oxygen-type dislocation loops are seen in the peripheral region compared to 2.0 MeV electrons.

At 673 K, growth behavior is slow and only perfect type of dislocation loops are seen in the irradiated area as shown in Fig. 4.17. Perfect loops coalesced at higher fluences and developed to dislocation lines which were stabilized at further irradiation.

Large defects with strong strain contrast, probably same with oxygen-type dislocation loops, were formed and burst at the upper-right part of the peripheral region of the irradiated area. Irradiation with further higher temperature at 773 K (Fig. 4.18) was found to produce only perfect type dislocation loops as same with the result of 3.0 MeV electron irradiation, which were increased in number and size with higher fluences.

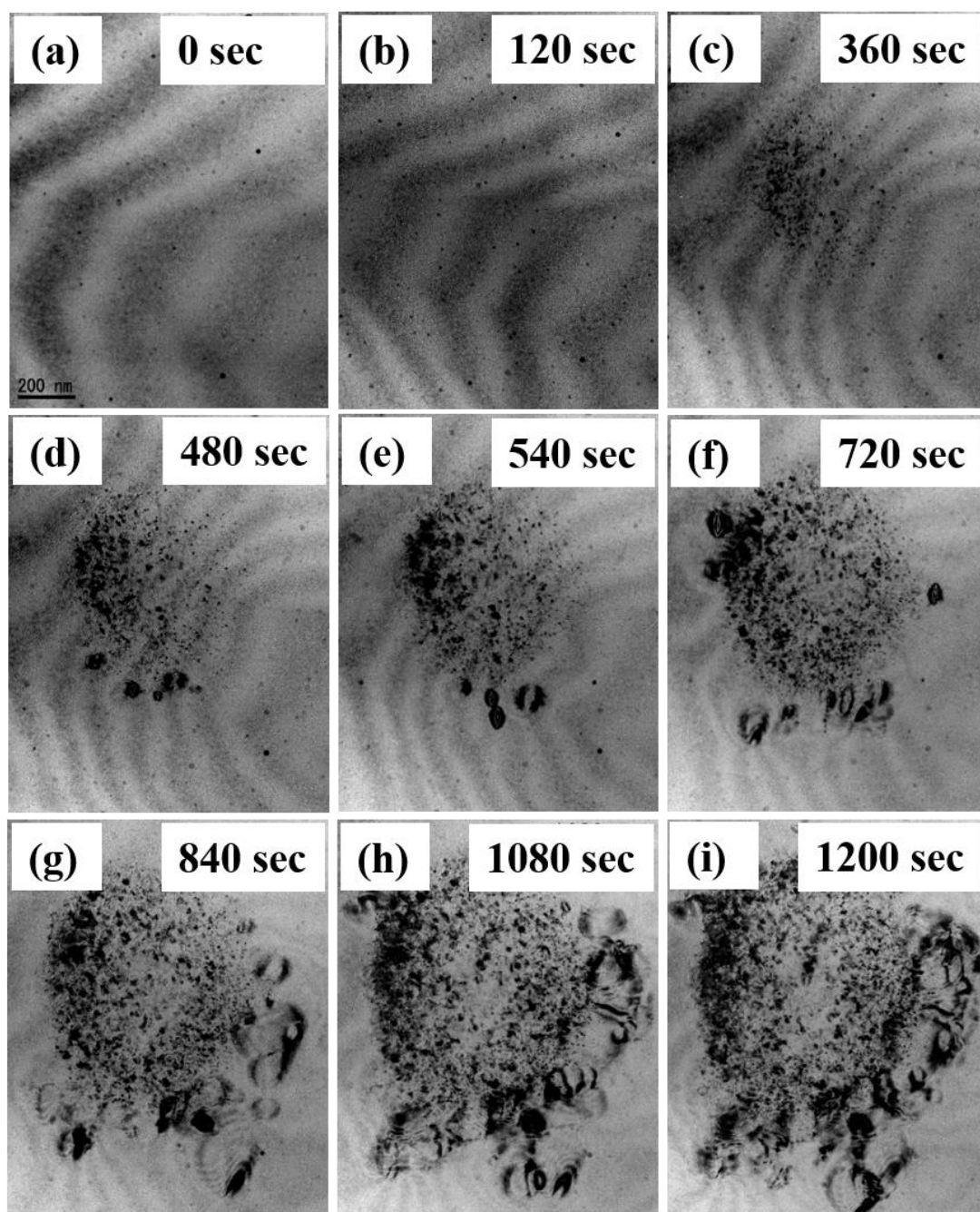


Fig. 4.15: Sequential BF-TEM image showing the defects nucleated in YSZ poly-crystals irradiated with 2.5 MeV incident electron at 300 K until $2.4 \times 10^{27} \text{ m}^{-2}$. The observations were performed from the [011] direction with $g = 111$ reflection. The dot contrasts at the un-irradiated and irradiated matrices were examined to be contaminations during ion milling process.

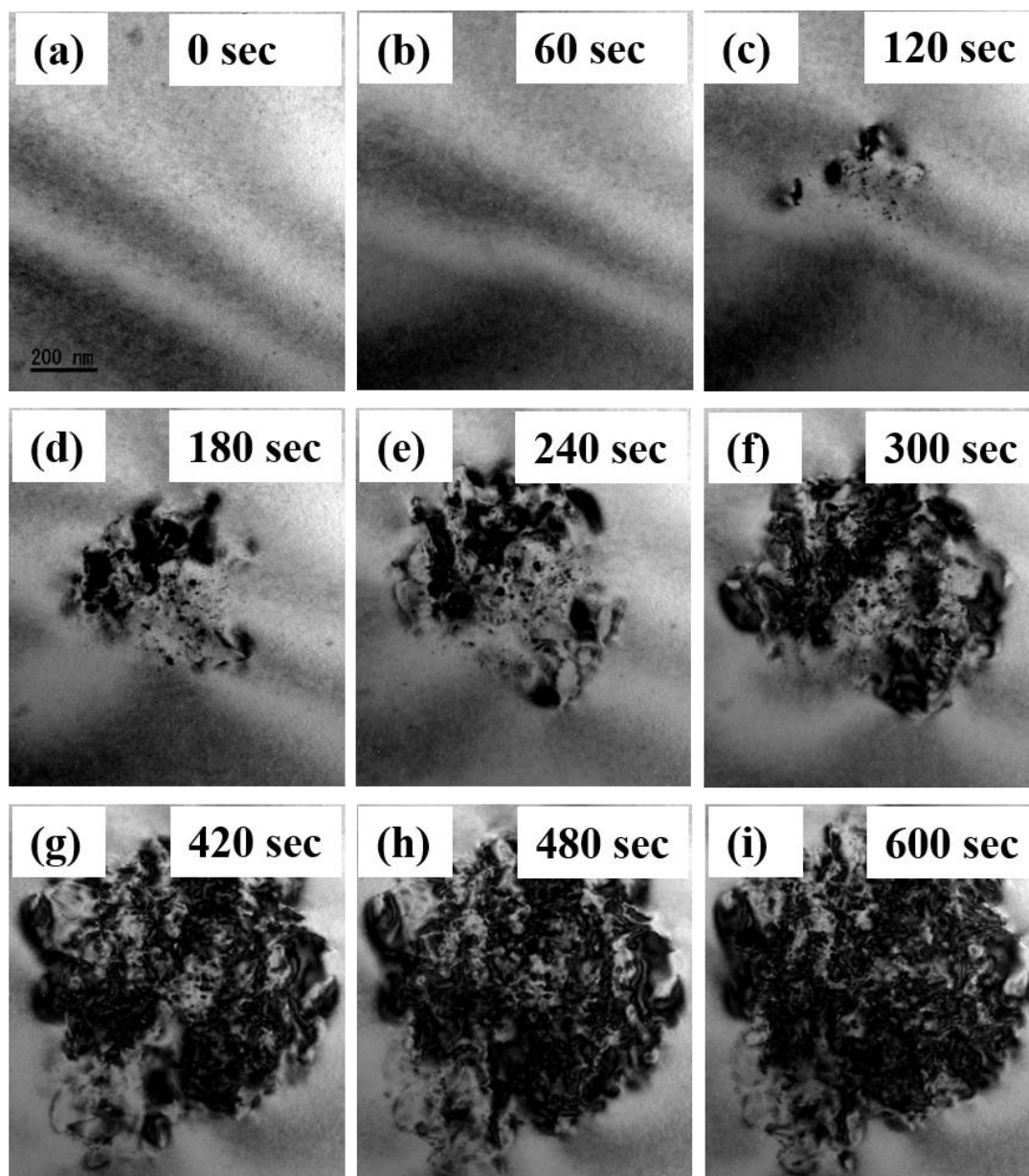


Fig. 4.16: Sequential BF-TEM image showing the defects nucleated in YSZ poly-crystals irradiated with 2.5 MeV incident electron at 573 K until $7.8 \times 10^{26} \text{ m}^{-2}$. The observations were performed from the [011] direction with $g = 111$ reflection.

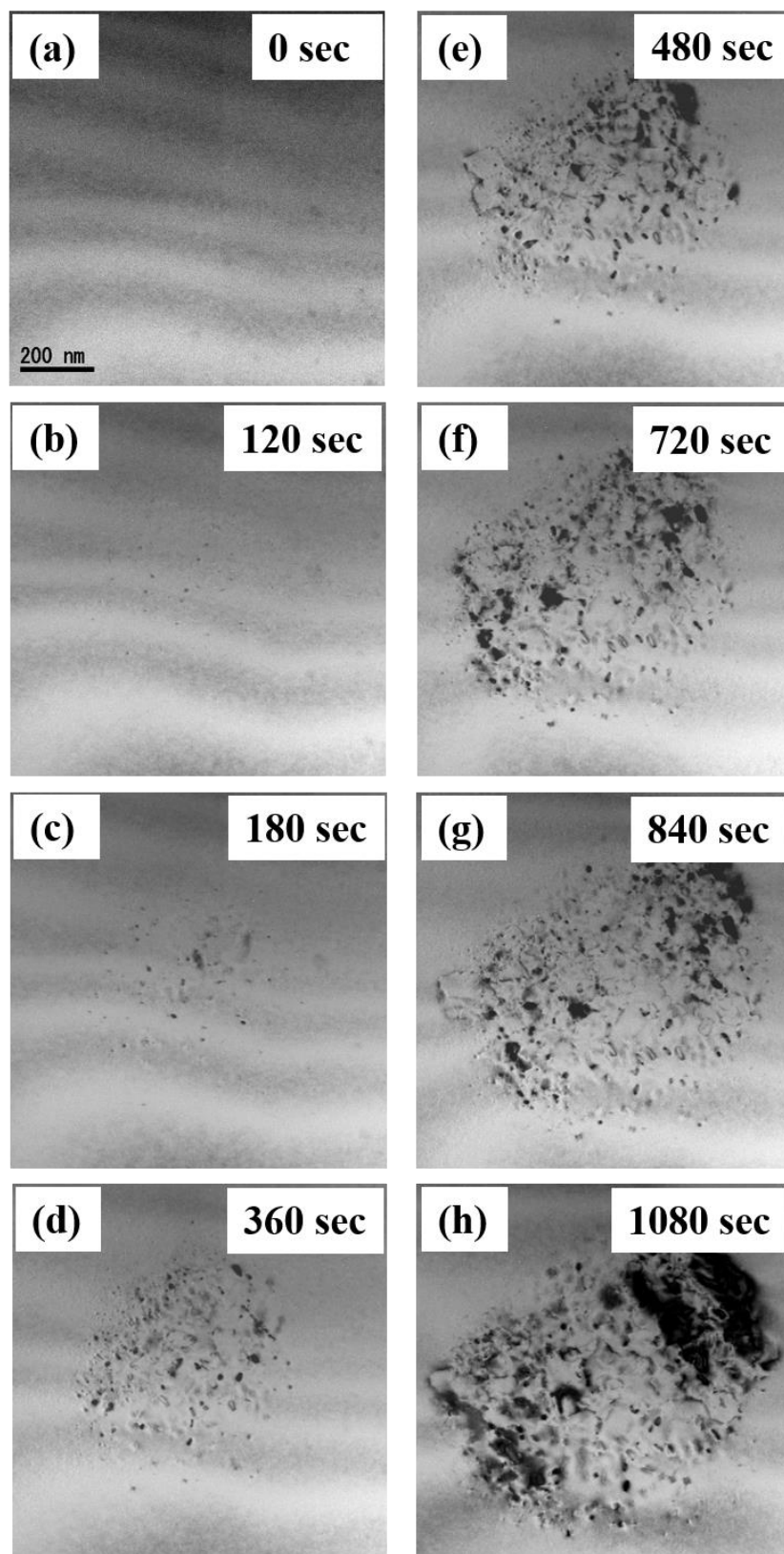


Fig. 4.17: Sequential BF-TEM images showing the defects nucleated in YSZ poly-crystals irradiated with 2.5 MeV incident electron at 673 K until $2.1 \times 10^{27} \text{ m}^{-2}$. The observations were performed from the [011] direction with $\mathbf{g} = 111$ reflection.

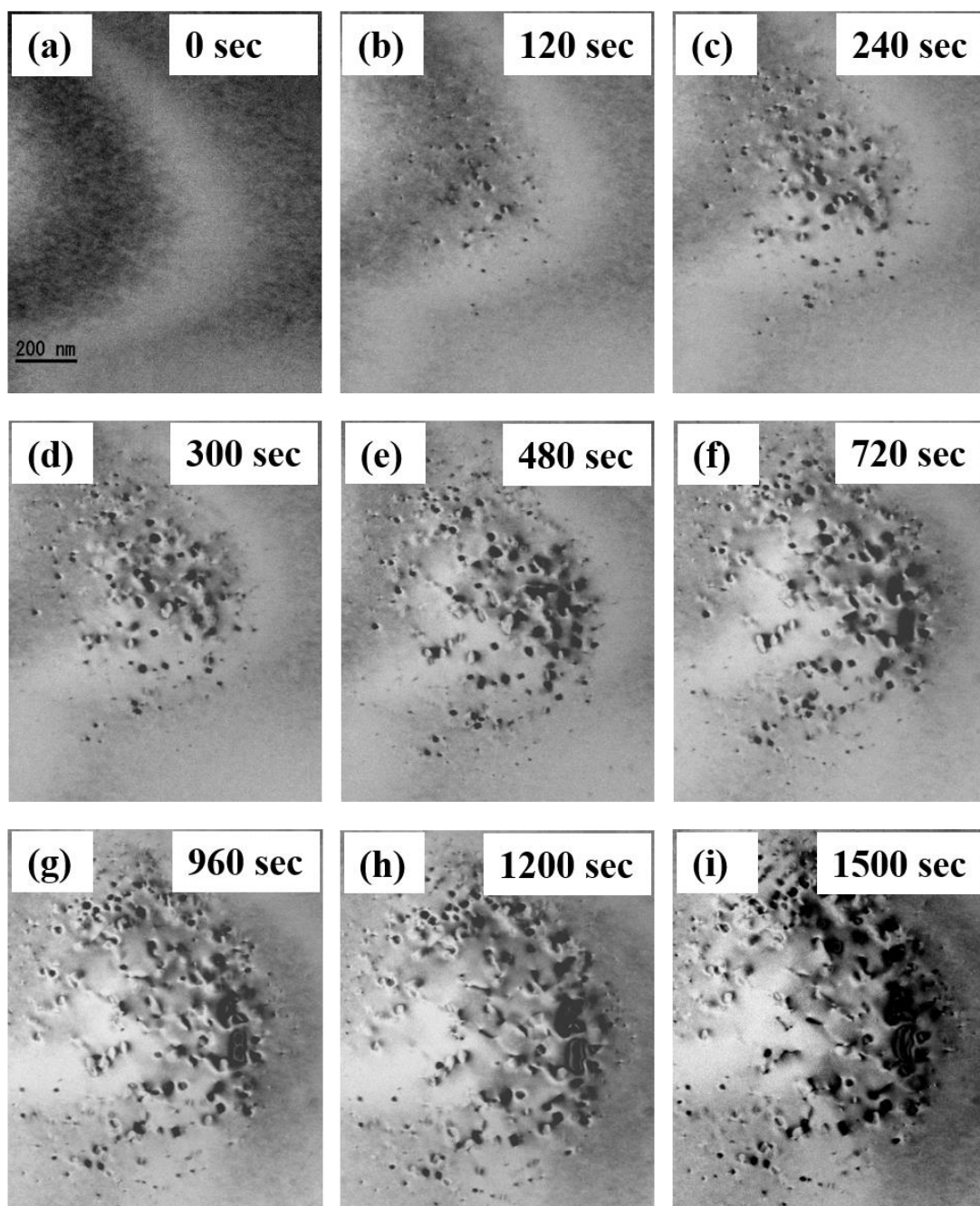


Fig. 4.18: Sequential BF-TEM image showing the defects nucleated in YSZ poly-crystals irradiated with 2.5 MeV incident electron at 773 K until $3.0 \times 10^{27} \text{ m}^{-2}$. The observations were performed from the [011] direction with $\mathbf{g} = 111$ reflection.

4.4 DISCUSSION:

It was found from *in situ* electron irradiation experiments with different energies and temperatures that two types of defect clusters are nucleated and grown on the matrices. Fig. 4.19 shows the summary of features of the defects described in Fig. 4.3 ~ 4.18 as a function of electron energy from 1.5 to 3 MeV and irradiation temperature from 300 to 773 K. On the other hand, Fig. 4.20 shows similar defect clusters unfolded at three non-identical irradiation conditions materializing the role of electron energy and irradiation temperatures in defect formation mechanism. Fig. 4.21 is a schematic diagram to show the comparison of extended defects nucleated and grown at different irradiation conditions. Hence it's clear that systematic *in situ* experiments on the evolution of dislocation loops in 8 mol% pristine YSZ specimen under high energy electron irradiation at different temperatures concede us to discuss several issues on the evolution of dislocation loops and change of microstructures under different irradiation conditions. However, at first, it's worthy to identify the type of loops. Then, discussion on the threshold displacement energy in YSZ will be described based on the results in the present work and literature [2, 36-39]. Finally, role of electron energy and irradiation temperature in evolution of dislocation loops will be described.

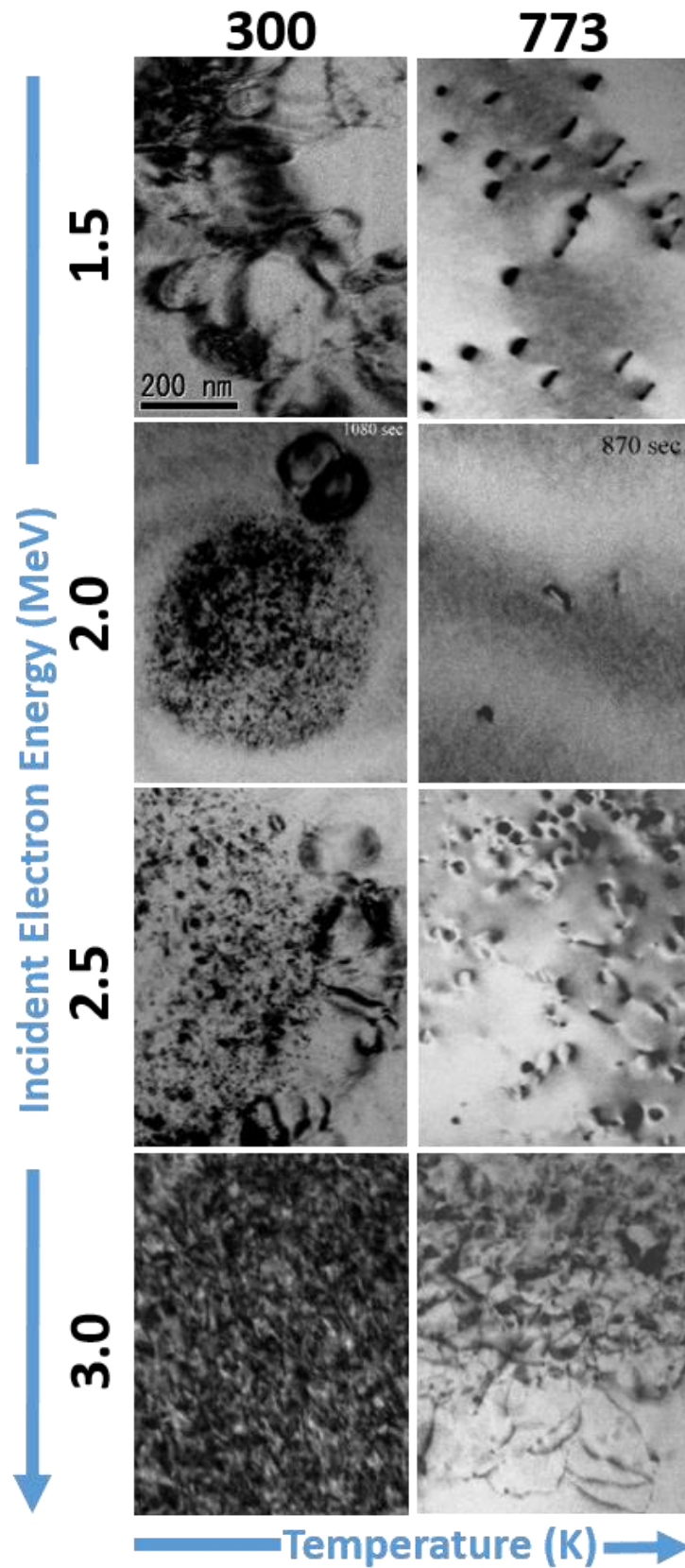


Fig. 4.19: BF-TEM images showing the features of the defects nucleated in YSZ polycrystals irradiated with 1.5 to 3.0 MeV incident electron at 300 to 773 K

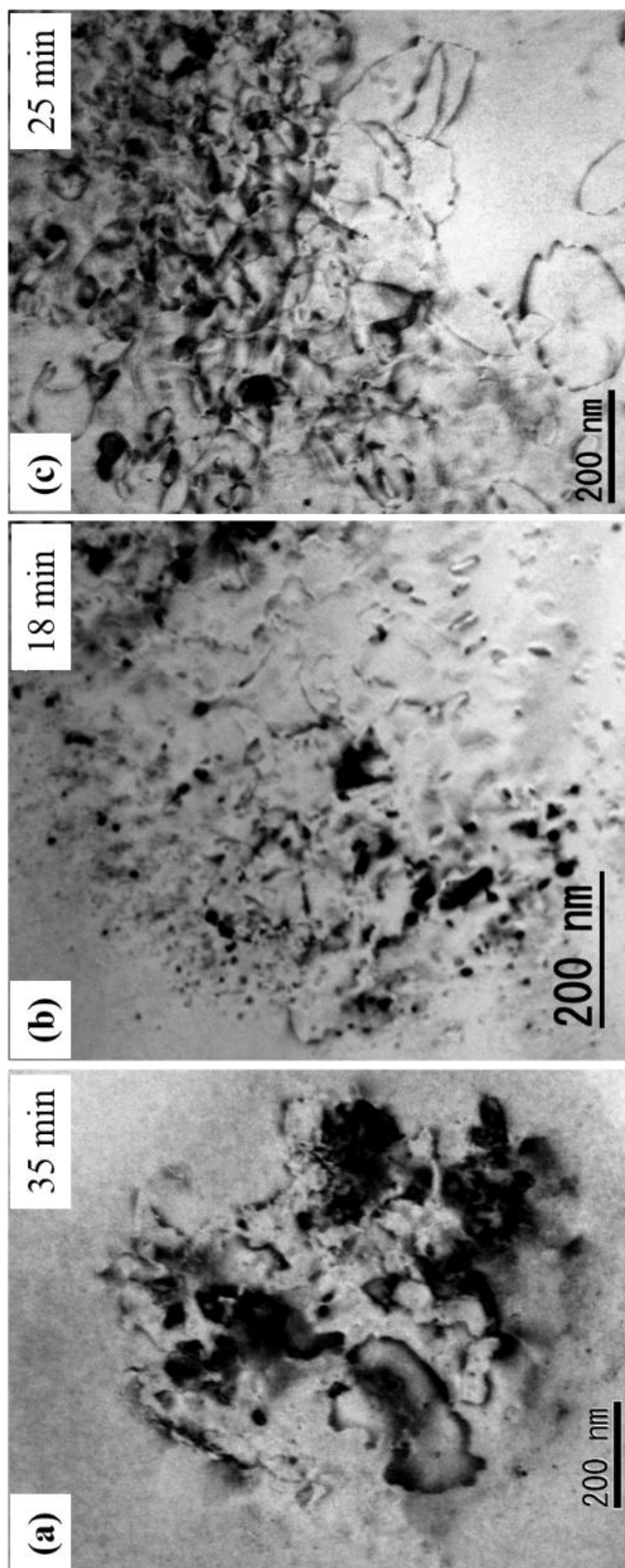


Fig. 4.20: BF-TEM images showing the defects nucleated in YSZ poly-crystals irradiated with (a) 1.5 MeV incident electron at 573 K, (b) 2.5 MeV incident electron at 673 K and (c) 3.0 MeV incident electron at 773 K at $2.3 \times 10^{27} \text{ m}^{-2}$, $2.1 \times 10^{27} \text{ m}^{-2}$ and $2.0 \times 10^{27} \text{ m}^{-2}$ respectively.

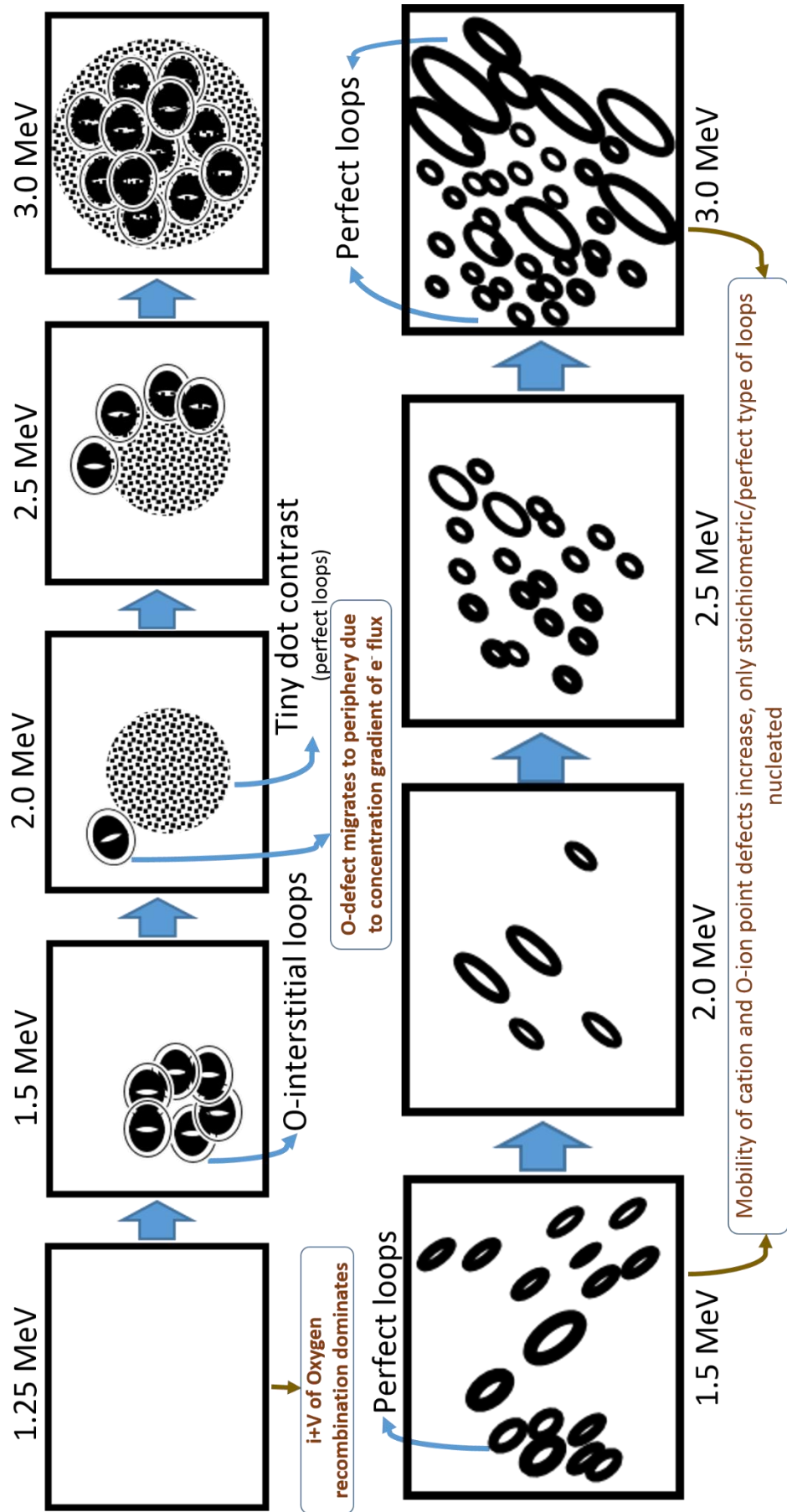


Fig. 4.21: Schematic illustration showing defects nucleated in YSZ under different irradiation conditions. Top row shows the defects at 300 K and the lower one shows defects at 773 K. Incident electron energies are shown at respective drawing in the illustration.

4.4.1 Characterization of Dislocation loops ($g \cdot b$ analysis):

Analyzing the defects nucleated in Fig. 4.3 – 4.16, it is obviously understood two different type of dislocation loops are formed except some diffuse dots which do not display a specific Burgers vector. The big loops with strong strain contrasts are discussed in this study as oxygen interstitial type dislocations as those are analogous to the previously reported defects lying on $\langle 111 \rangle$ planes [19]. This speculation is also supported by a theoretical calculation of YSZ, which reveals stronger stress and strain fields prevailing around an oxygen platelet than a neutral dislocation loop [40]. The loops at higher irradiation temperature are analyzed using the invisibility criterion $|g \cdot b| = 0$ [41]. When $(g \cdot b)s > 0$, dislocation loops show outside contrast; $(g \cdot b)s = 0$, dislocation loops are invisible; $(g \cdot b)s < 0$, dislocation loops show inside contrast, where s is the magnitude of reciprocal space vector representing the deviation from the exact reflecting position. The loops indicated by white and blue arrow in the fig. 4.22 (a), (b) and (c) are visible under two diffraction conditions of $g = [111]$ and $[012]$, and becomes invisible when $g = [011]$. Hence Burgers vectors of the loops are identified as parallel to $[011]$ which is in good agreement with dislocation loop nature of UO_2 under fission damage [42, 43]. However, current $g \cdot b$ analysis is not sufficient to certainly determine the type of the loops, and more work is needed in the future.

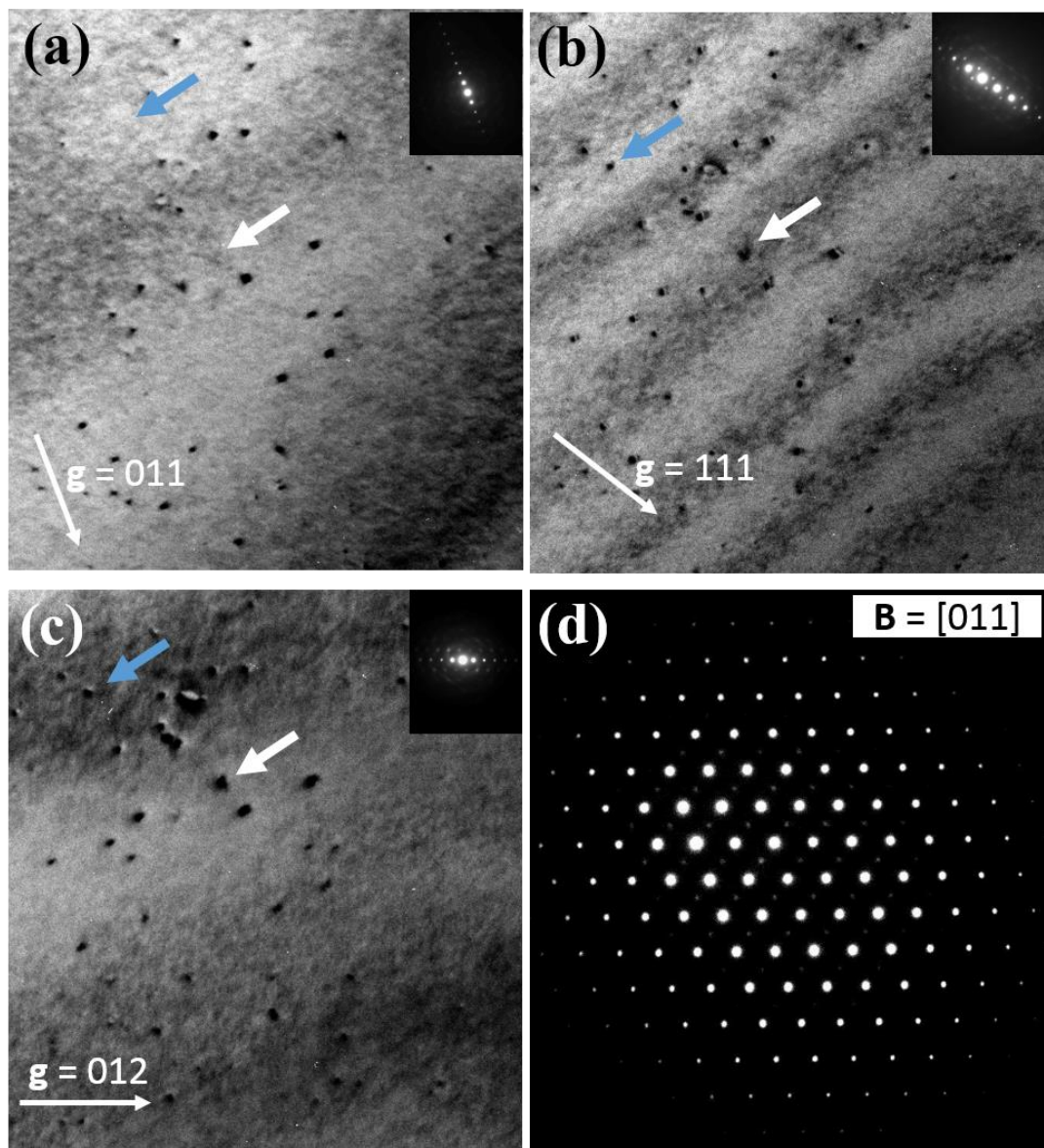


Fig. 4.22: Series of BF-TEM images used for dislocation loop characterization in YSZ with 3.0 MeV electron irradiation at 773 K at a dose of $3.0 \times 10^{26} \text{ m}^{-2}$. The beam direction is shown in (d) and the direction of g are inserted in respective images ((a)-(c)). Blue and white arrows indicate the loops discussed in the text.

4.4.2 Threshold Displacement Energy (E_d) Estimation:

In situ electron irradiation has been a powerful tool on radiation damage study for decades, which allows us to determine the value of displacement energy (E_d) at an accelerating voltage where visible extended defects (usually dislocation loops) are observed. In the case of ceramic compounds having multiple sublattices and elements, all the sublattices should be displaced to form visible and stable defect clusters if the defects possess the stoichiometric composition [44]. For this reason, displacement energy of the massive atomic sublattice or the one with higher value of E_d can be determined by the minimum electron energy for dislocation loops formation. However, in the case of YSZ, as has been shown in the present study, the nature of dislocation loops formed under electron irradiation depends on electron energy from 1.5 ~ 3.0 MeV and temperature from 300 ~ 773 K. Furthermore, the nature of defect clusters is either with stoichiometric composition or nonstoichiometric one. It is, therefore, not straightforward to determine the displacement energy in YSZ.

According to the calculation by Mackinley-Feschbach formula, the displacement of oxygen starts from around 0.25 MeV with an assumption of 40 eV as the value of E_d for oxygen sublattice. It is worth to note here that reported values of E_d for oxygen sublattice are largely dependent on researchers and evaluation technique. Xiao *et. al* [36] showed by ab initio molecular dynamics simulations that the minimum value of

E_d for oxygen ions is 14 eV along $\langle 100 \rangle$ direction, and more than 100 eV, as the highest, along the direction of $\langle 111 \rangle$, and along other directions, such as $\langle 110 \rangle$ and $\langle 112 \rangle$, are around 30 eV. Costantini et. al. [24, 37] reported the displacement energy for O sublattices by optical absorption measurement in YSZ both with 9.5 mol% or 18 mol% Y_2O_3 to be more than 200 eV. Yasuda *et. al* [19] also observed the nucleation-and-growth of oxygen type defects under 200 keV electron irradiation in ion-irradiated YSZ, which leads the value of E_d for oxygen to be 33 eV by the following equation between E_d of a sublattice and incident electron energy of (E_e).

$$E_d = \frac{2E_e(E_e + 2m_e c^2)}{mc^2} = \frac{2147.7E_e(E_e + 1.022)}{A}, [\text{eV}] \quad (4-1)$$

Where, E_d is in the unit of eV, E_e is the electron energy in MeV and A is the atomic mass of the target ion in amu.

One explanation for the large discrepancy of the values of E_d for oxygen sublattice is whether the displaced oxygen ions are stable or not. Due to the presence of a high concentration of oxygen vacancies in the matrix, most of the oxygen interstitials are eliminated by the instantaneous recombination with the structural vacancies. Optical measurements might detect the stable defects after the recombination, while the simulation can detect the single (or initial) displacement prior to recombination. And it also explains the results that up to 1.25 MeV we do not

observe defect clusters in pristine specimens, although defects were grown in ion-irradiated specimen [19]. That suggests that oxygen interstitials produced by the recoil effectively annihilate at the structural vacancies, which in turn may contribute to dynamic annealing on the cation sublattice due to strong ionic interaction [45]. When we apply the estimation of the displacement of O sublattice with equation (4-1) under the assumption of 1.25 MeV for the stable defect formation, a value of ~ 380 eV is obtained as the threshold displacement energy. This value is much higher than that proposed by Costantini *et. al.* [24, 37], which is 200 eV but still O displacement is found unstable due to the recombination with structural vacancies. It is also noted that few works reported decreasing trend of threshold displacement energy with increasing irradiation temperature [44, 46] for metal and ceramic which may be due to the change of acceleration of defect aggregation [47]. The difference in temperatures might be attributed to the discrepancy between reports (simulations are often performed at 0 K). It is difficult to discuss on this effect at this moment.

As we discussed above, the oxygen sublattice is supposed to displace at around 0.25 MeV electron irradiation (Fig. 4.1), and the electron energy beyond 1.25 MeV is needed to form defect clusters in YSZ. Defect clusters, oxygen-type dislocation loops, were formed at 1.5 MeV electron irradiation with different irradiation temperatures. As already discussed in 4.3.4, the formation of oxygen type

defects with 1.5 MeV is suggesting the displacement damages in cation sublattices, which may stabilize the oxygen defects to form defect clusters in the matrices due to strong ionic interaction exists between oxygen and cation sublattices. The threshold electron energy to induce displacement damage in cation (Zr) sublattice is, therefore, determined between 1.25 and 1.5 MeV. Using equation (4-1), the threshold displacement energy, E_d for Zr-cation is determined to be in the range of $66 < E_{d,Zr} \leq 89$ in eV. This value is obtained experimentally by in situ observations in TEM. This value is comparable with the previously reported E_d values of 80 eV obtained by optical absorption [37] and molecular dynamic simulation [24] for Zr sublattice in YSZ.

4.4.3 Role of e^- Energy and Flux Distribution:

Electron irradiation at 1.25 MeV did not produce any defect clusters (Fig. 4.2) in pristine YSZ specimen, whereas we got different types of defect aggregation at all irradiation conditions at and above 1.5 MeV electron (Fig. 4.3 – 4.18) until 3.0 MeV. Mislaying of the defect clusters at 1.25 MeV suggests the recombination of displaced oxygen interstitials with structural vacancies incorporated for charge compensation [45, 48] due to the substitution of Zr^{4+} ions by Y^{3+} dominates defect formation behavior at this irradiation energy. Analyzing the sequential images of the defects at

different irradiation conditions at and beyond 1.5 MeV, it is obvious that the size and density are increasing in size with increasing electron energy. At lower electron energy (1.5 MeV), the knocked-on displacement rate of O is much higher than that of cation and this difference in displacement rate causes only oxygen type of dislocation to be formed. Though the threshold displacement energy is higher for cation (~ 80 eV determined in this study), Zr sublattice is also anticipated (Fig. 4.1), which did not produce point defects but contributed to the production of large oxygen loops. Here Zr displacements exerted strain [12] to the lattice structure to create nucleation sites for oxygen defects. Here it is noted that some oxygen type loops moved to the peripheral region with higher fluences. But irradiation with 2.0 MeV caused higher displacement rate of both of O and cation and small perfect type of dislocation loops are formed with increasing trend in size and number with higher fluences. The large loop with around 200 nm size at the periphery, as it is analogous to the structure described in Ref. [19], is confirmed as oxygen displacement type loop, and the reason for migration to the peripheral region may be due to the concentration gradient of the electron flux. Fig. 4.23 shows measured electron flux at an energy of 1.5 MeV and a nominal flux (measured flux at the central part of the beam) of $1 \times 10^{24} \text{ m}^{-2}\text{s}^{-1}$. The measured focused electron beam has a diameter of around $1 \sim 1.5 \text{ }\mu\text{m}$ (Fig. 4.24). The curve shown in Fig. 4.25 is the fitted result by using a Gaussian distribution by the

following equation:

$$y = y_0 + \frac{A}{w\sqrt{\pi}/2} e^{-2\frac{(x-x_c)^2}{w^2}} \quad (4-2)$$

The value of FWHM was evaluated to be around 0.6 μm . The displacement rate (dpa/s) is considered to be proportional to electron beam flux. The flow of point defects ($J = -dC_i/dx$) is, therefore, proportional to the gradient of the flux profile shown in Fig.4.25, where C_i is the concentration of point defects of i species and x is the distance. This is attributed to cause the displaced point defects (especially, oxygen defects with a higher mobility) to move to the periphery of the focused electron beam. Same trend of defect evolution sustains in the higher electron energies also at 2.5 and 3.0 MeV with an increment in number and size of loops.

The experimental results draw attention to the importance displacement rate of O and cation sublattices and their ratios for the microstructure evolution in pristine YSZ. Fig. 4.26, 4.27 and 4.28 shows displacement per atom (dpa) for O, Zr and ratio of dpa (Zr/O) as a function of incident electron energy at some reported threshold displacement energies for O and Zr respectively, which show the dpa and ratio of dpa varies with increasing irradiation energy leading to the non-identical defect formation behavior at a specific irradiation temperature. The role of irradiation temperature for evolution of defect clusters will be discussed in the next section.

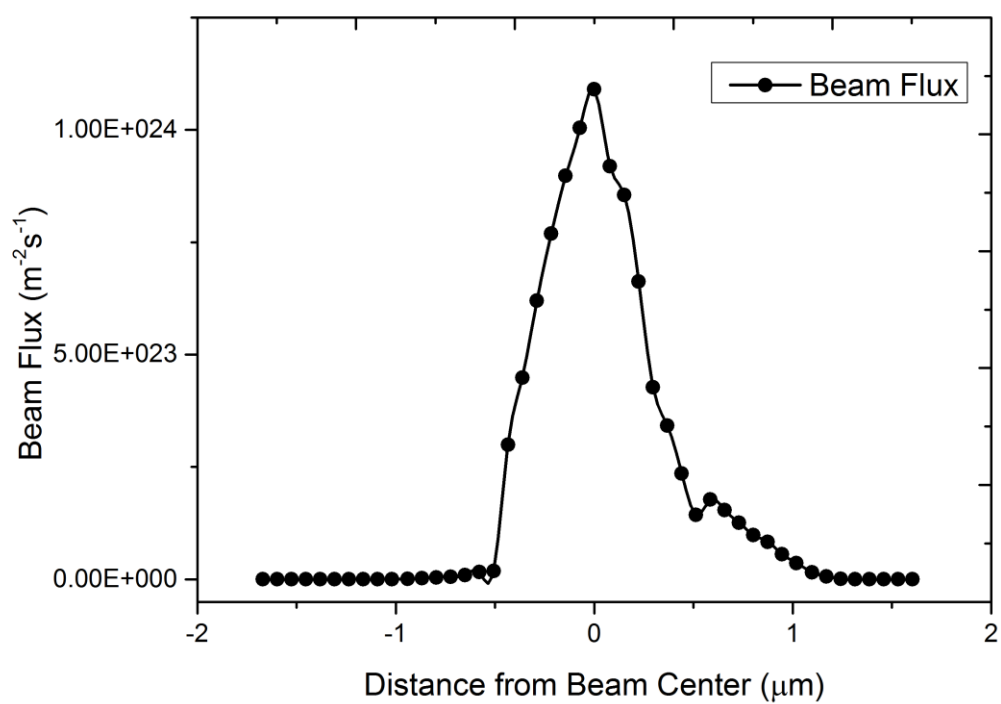


Fig. 4.23: Nearly Gaussian shaped flux distribution of incident electron beam. The measurement was performed with 1.5 MeV incident electron at Ultra-High Voltage Electron Microscope (Hitachi H-3000).

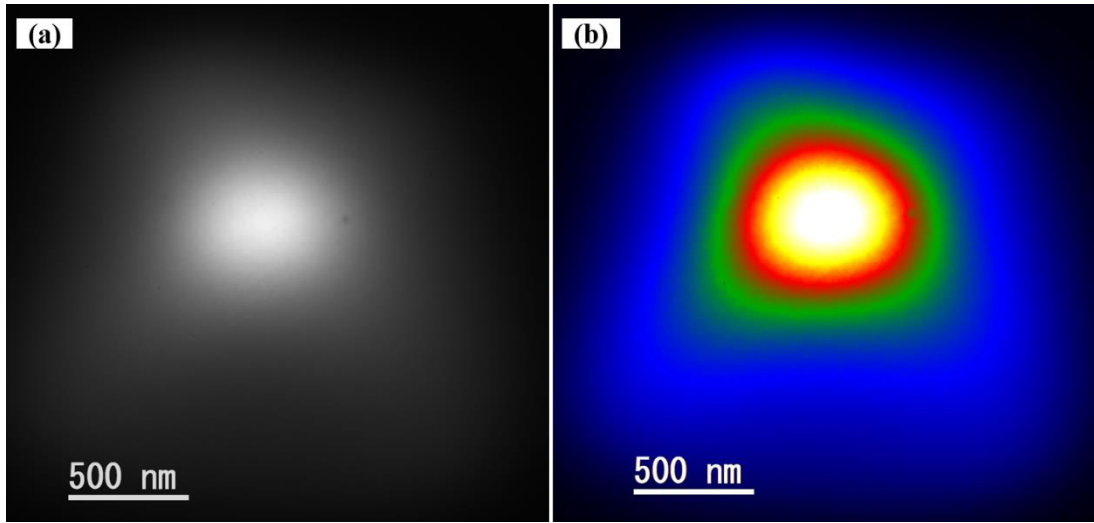


Fig. 4.24: Typical electron beam used for this work. The image taken with 1.5 MeV incident electron at Ultra-High Voltage Electron Microscope (Hitachi H-3000). (a) Shows the actual beam and (b) shows the intensity of the beam, the most intense region is in the center with white/yellow color.

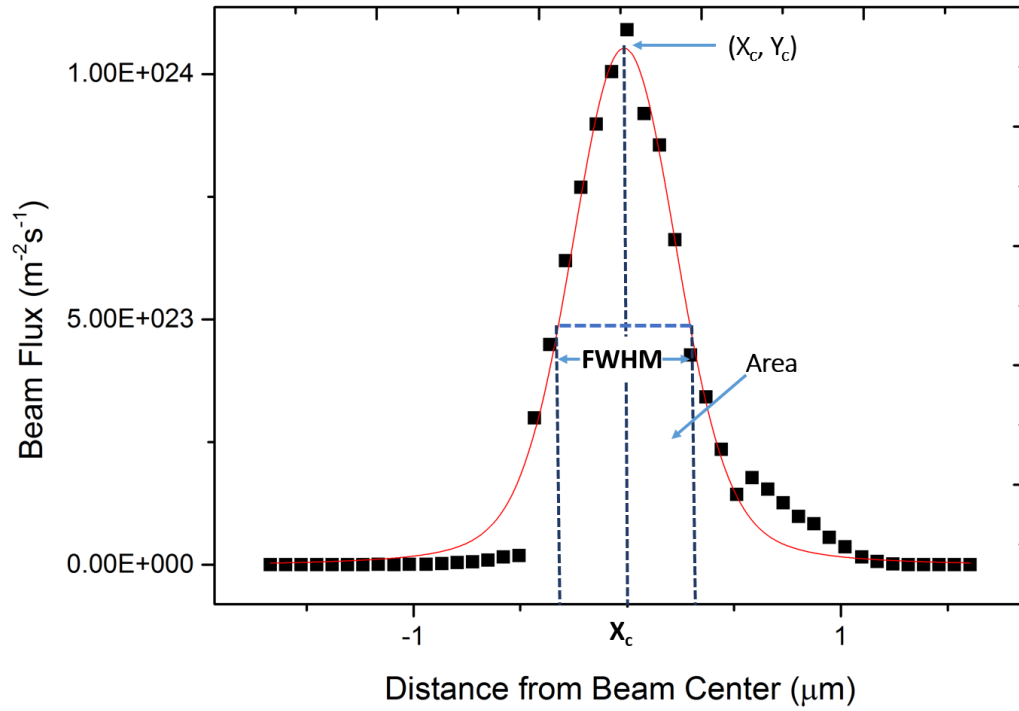


Fig. 4.25: Flux distribution of incident electron beam fitted with Gauss function.

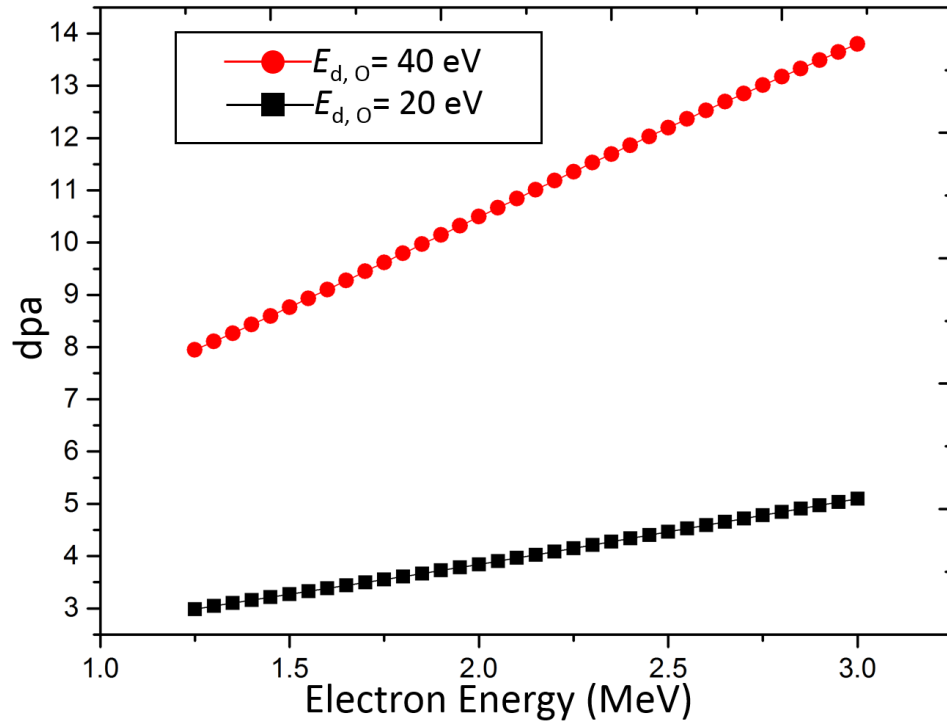


Fig. 4.26: Displacement per atom (dpa) as a function of incident electron energy for O sublattices in YSZ assuming E_d as 40 and 20 eV at an electron fluence of $2.4 \times 10^{27} \text{ m}^{-2}$.

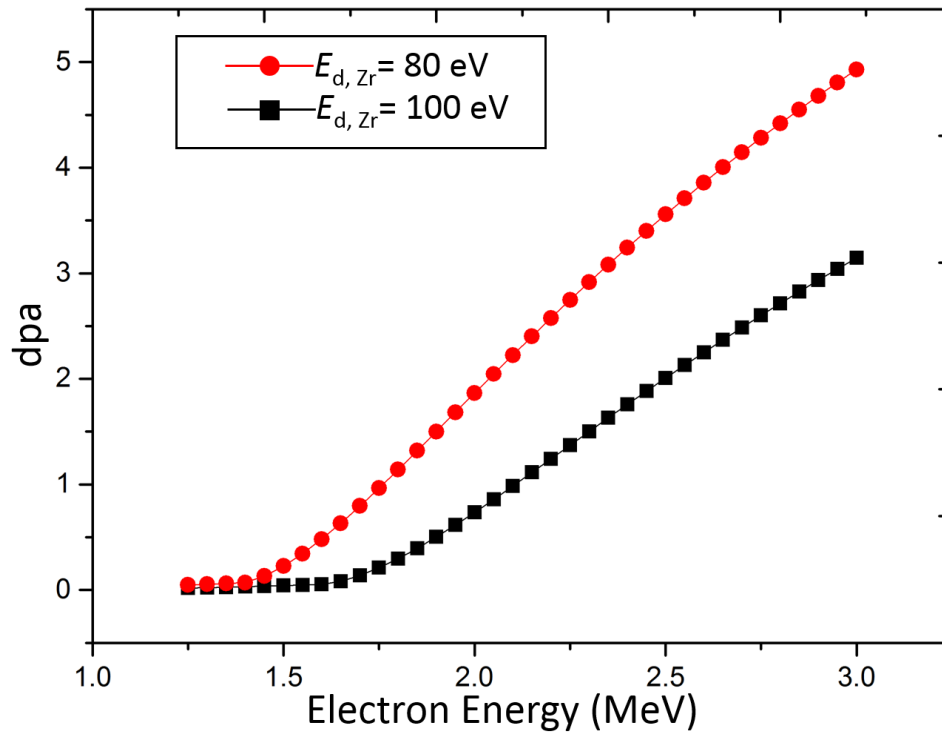


Fig. 4.27: Displacement per atom (dpa) as a function of incident electron energy for Zr sublattices in YSZ assuming E_d as 80 and 100 eV at an electron fluence of $2.4 \times 10^{27} \text{ m}^{-2}$.

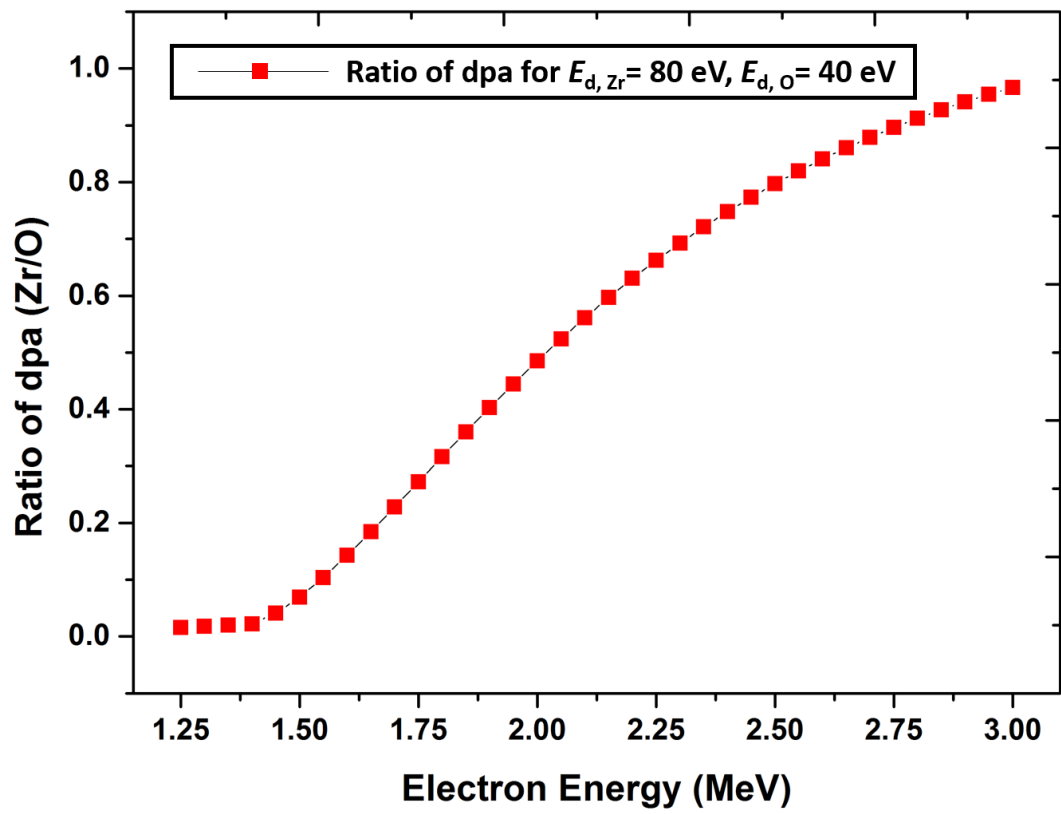


Fig. 4.28: Ratio of displacement per atom (dpa) for Zr and O sublattices in YSZ assuming E_d for Zr to be 80 eV and O to be 40 eV.

4.4.4 Role of Irradiation Temperature:

Irradiation temperature is also a very important factor along with irradiation energy, and controls the mobility of interstitial and vacancy of the anion and cation sublattices of irradiated materials and evolution of point defects and defect clusters [49]. The nucleation and growth of defect clusters and dislocation loops are dependent on several factors, such as productivity, survivability and mobility of point defects [21, 50], and among them ‘mobility’ is greatly influenced by irradiation temperature. Here the ‘mobility’ of i species is the term expressed by a cross of the concentration and diffusivity of i species, and, therefore, it is different from cations and anions, and also vacancies and interstitials of constituting species of the material. The migration energy of ZrO_2 was shown in Table 2.2 (section 2.5 in chapter 2), and the migration energy of cations are much higher than anions.

In the present study with 8 mol % YSZ specimen, we found quite different microstructure at different irradiation temperatures at a same irradiation energies (Fig. 4.21). At a lower irradiation temperature, such as 300 K, the mobility of cation point defects are significantly low (due to the high migration energy), and therefore, the O-interstitials dominating the defect formation mechanism, which is completely in agreement with the lower migration energy of anion sublattices [26]. But with increasing irradiation temperatures the ratio of displacement damages changes and the

displaced interstitials and vacancies of anion and cation sublattices mobilize differently. In the lower temperature case (300 K), as the mobility is lower, the interstitials of displaced atoms form defect clusters at the central part of incident beam. And at higher temperatures (573, 673 and 773 K) the recombination of interstitials and vacancies increases along with formation of stoichiometric perfect dislocation loops. Even-though the migration energies of vacancies are higher, mutual annihilation between two kinds of defects slows down the increment of vacancy concentrations and contemporarily the displaced interstitials are annihilated at their sinks such as specimen surfaces [49]. The defects are obviously not accumulated homogeneously as they are partly dependent on mobility of interstitials and vacancies of different species which are quite different at different temperatures and the localization of preferred surface sinks as well [34].

At high temperature, such as 773 K, only perfect dislocation loops are formed. This is presumably because the mobility of oxygen interstitials and vacancies are high enough to annihilate at sinks (such as surface) to form oxygen-type dislocation loops. The threshold temperature, T_c , to nucleate only perfect loops was found to be dependent on electron energy. Namely, T_c is evaluated to be 573, 673 and 773 K for irradiation energy with 1.5, 2.5 and 3.0 MeV respectively. Hence, T_c is increasing with increasing incident electron energy.

Hojo *et. al.* [51] showed that He or Xe ion irradiation at high temperature (1073, 1273 and 1473 K) forms bubbles in YSZ single crystals irrespective of ion species and irradiation temperatures. However, they showed that loop formation depends on ion species and irradiation temperatures [52, 53]. This is may be due to the shifting of damage fraction to lower fluences at increasing temperature irradiations [7, 54]. The radiation damage at different irradiation conditions follow a multistep damage accumulation (MSDA) model each one triggered by destabilization of the current form [55, 56]. But surprisingly at the third step at high fluences with high irradiation temperature we observed a decrease in the damage nucleation and a very slow increment of loop size only (Fig. 4.29). Higher temperature provides higher defect mobility and enhanced defect clustering to form denser and/or bigger dislocation loops but at the same time higher mobility of interstitials and vacancies may lead to higher interstitial-vacancy recombination along with disappearances at surface sinks. Moreover, perfect loops act as efficient sink for point defects leading to the annihilation of newly formed radiation defects. Hence it is very obvious to observe only a very slow increment in size of dislocation loops with higher fluences at increasing irradiation temperatures with 3.0 MeV electron irradiation.

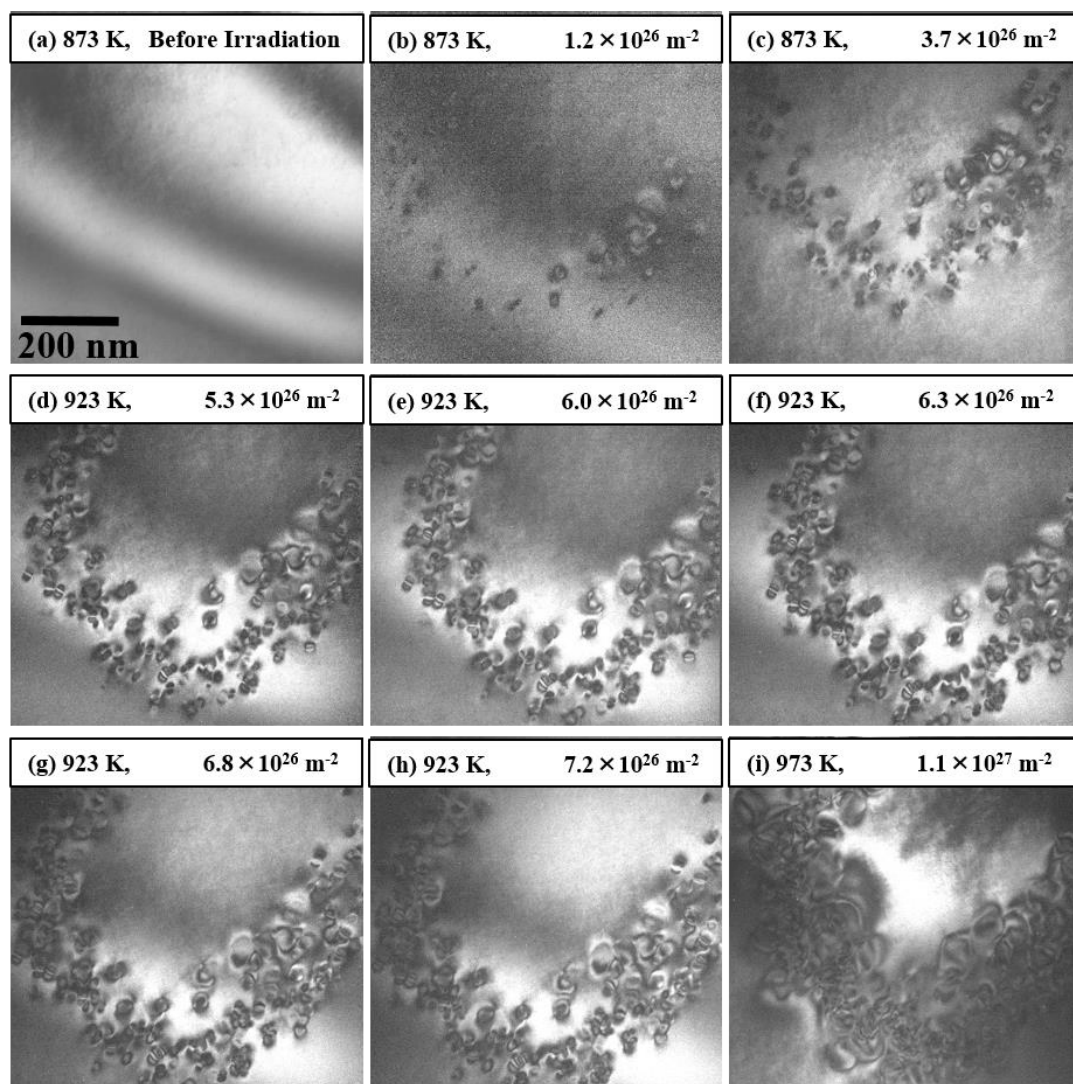


Fig. 4.29: BF-TEM images showing the defects nucleated in YSZ poly-crystals irradiated with 3.0 MeV incident electron at 873 - 973 K. The respective fluences of incident electron are mentioned in each micrograph. The observations were performed from the [011] direction with $\mathbf{g} = 012$ reflection.

4.5 CONCLUSIONS:

A systematic series of experiments with 8 mol % pristine yttria-stabilized zirconia at different irradiation conditions led us to conclude some important issues as following in the nucleation-and-growth process of radiation induced defects.

- (1) Electron energy below 1.25 MeV is not enough to form defect clusters due to the interstitial-vacancy recombination at structural vacancy of oxygen sublattice.
- (2) Two types of extended defects, that is, perfect dislocation loops (stoichiometric composition) and/or oxygen interstitial-type ones (non-stoichiometric composition), were formed at 1.5, 2.0, 2.5 and 3.0 MeV electron irradiations, depending on electron energy and irradiation temperature.
- (3) The threshold displacement energy for Zr sublattices is bracketed as $66 < E_{d,Zr} \leq 89$ in eV, which is comparable with previously reported values.
- (4) The ratio of the displacement damage in O and cation sublattices, induced by the incident electron energies are discussed as the principal factor for controlling the evolution of dislocation loops.
- (5) Irradiation temperature plays a very important role in nucleation-growth and stabilization of dislocation loops. Though temperature as low as 573 K is sufficient to accelerate the disordering process to nucleate perfect dislocation loops, this temperature value found increasing with higher irradiation energies.

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Chapter 5

Defects in 8 mol% YSZ Irradiated with Electrons Subsequent to Irradiation with 200 MeV Xe Ions

Science walks forward on two feet, namely theory and experiment...but continuous progress is only made by the use of both.

*-Robert A. Millikan
(1868 - 1953)*

5.1 INTRODUCTION:

The importance of yttria-stabilized zirconia to be used in research, both theoretical and experimental, is explained in detail in the earlier chapters. Despite years of application of YSZ and CeO₂ as a surrogate material to UO₂, ThO₂ and PuO₂ [1, 2], to understand the microscopic insights of radiation damage, the mechanism responsible for the excellent radiation resistance is not fully understood until now. The nucleation and growth of microstructure in pristine YSZ specimens under different irradiation conditions is presented in chapter 4 with a discussion on a role of incident electron energy and irradiation temperature on the evolution of dislocation loops and the fundamental kinetic behavior of point defects. However, in the practical radiation environment of fuel and target materials, YSZ should withstand with a high radiation exposure consisting of different types and dose levels.

Radiation damage induced by fission fragments (FFs) having typical energies ranging from 70 - 100 MeV has shown to induce the most crucial issue for fuel or

target materials [3]. Those FFs induce ion tracks in fluorite structure oxide ceramics, such as UO_2 , CeO_2 and ZrO_2 due to the high density electronic excitation [4-9]. Ion tracks in those oxides has been found to maintain its crystal structure, but the core region of the ion tracks has a structure with depressed lower atomic density. Moreover, extensive irradiation to high fluences has shown the development of dislocation structure due to the overlapping of high density electronic excitation [7]. It is, therefore, important to investigate interactions between different types of defects, such as ion tracks and Frenkel defects, for the understanding of microstructure evolution in fuel and target materials. High energy electron irradiation induces displacements in the oxygen and cation sublattices in YSZ, as described in the previous chapters, and their interaction with ion-tracks induced by swift heavy ions is also an important issue to be investigated. The experimental outcomes with 3.0 MeV electron irradiation at different irradiation temperatures with pre-ion-irradiated YSZ specimen will be presented in this chapter with a goal to understand the stability of this radiation tolerant fluorite structure oxide ceramic in a better way.

5.2 MATERIALS AND EXPERIMENTAL PROCEDURE:

Yttria-stabilized cubic zirconia (YSZ) pellets were prepared by sintering of ZrO_2 containing 8 mol% Y_2O_3 powders supplied by Furuuchi Chemical Co. The

procedure for fabricating sintered body was described in detail in chapter 4. The sintered body was cut and polished mechanically to be disk specimens 3 mm in diameter and 150 μm in thickness, and those were irradiated with 200 MeV Xe^{14+} ions at an ambient temperature to fluence of 5×10^{11} ions/ cm^2 by using a Tandem accelerator at Tokai research center in Japan Atomic Energy Agency (JAEA). The electronic stopping power of 200 MeV Xe ions were evaluated by SRIM (Stopping and Range of Ions in Matter) code [10] to be 28 keV/nm at the sub-surface region of the specimen. The nuclear stopping power is, on the other hand, negligible to be 1.2 keV/nm. The irradiated specimens were mechanically dimpled at the centre, followed by conventional ion thinning with Ar-ions from the opposite side of the ion irradiated surface at a low temperature condition cooled with liquid nitrogen to prepare thin-foil specimen for TEM study. Ar-ion energy was decreased step by step to 0.5 keV to minimize the Ar-ion damage. *In situ* observation of the formation and evolution of dislocation loops under successive irradiation with 3.0 MeV electrons were performed on the ion irradiated specimens with 200 MeV Xe ions at different irradiation temperatures (300, 573 and 773 K) with an ultra-high voltage electron microscope (H-3000, Hitachi Ltd.) at Research Center for Ultra High Voltage Electron Microscopy (UHVEM) of Osaka University up to an electron fluence of $\sim 1.8 \times 10^{26}$ m^{-2} . The electron irradiation was performed by using a focused electron beam with a size of

around 1-1.5 μm in diameter, The nucleation and growth process were recorded *in situ* by bright-field (BF) TEM technique either with a diffraction vector of $\mathbf{g} = 111$.

5.3 RESULTS:

The pre-irradiated YSZ specimen was subjected to 3.0 MeV electron irradiation at three different irradiation temperatures, namely 300, 573 and 773 K, and different types damage evolution were recorded dependent on the temperature. Results are compared to the microstructure evolution of the pristine YSZ specimen, and the role of sinks are discussed.

5.3.1 Irradiation at 300 K

It has been shown in literatures that swift heavy ions with high electronic stopping induce continuous cylindrical defects, called ion tracks, in fluorite structure oxides, such as UO_2 , CeO_2 and YSZ. The threshold value for the formation of continuous ion tracks is known to depend on materials, ranging from around 10 to 30 keV/nm. The threshold electronic stopping for YSZ is reported to be 20-30 keV/nm in the low velocity regime [11].

Fig. 5.1 shows *in situ* TEM images of the defects nucleated in 8 mol% xenon ion-irradiated YSZ poly-crystals under 3.0 MeV electron irradiation at 300 K. The BF

images were taken at a diffraction condition of $\mathbf{g} = 111$, and the electron beam was close to $\mathbf{B} = [110]$. Small but a high density of oxygen type dislocation loops were observed at a very low fluence of $3 \times 10^{23} \text{ m}^{-2}$ over the irradiated region, and the size of the loops increases with increasing fluences. The microstructure is significantly different from the pristine YSZ specimen under the same condition of electron irradiation, where small perfect loops and large oxygen-type loops were formed simultaneously preferentially at the center part of the electron beam as shown in Fig. 4.9 (a). It is anticipated that ion tracks, induced by swift heavy xenon ions, whose core damage regions are characterized by a reduced atomic density, worked as preferential nucleation sites to accumulate the oxygen interstitials. Isolated oxygen interstitials might annihilate in the core damage regions and the excess of those interstitials move to equally distributed core damaged regions of ion-tracks to form oxygen-interstitial type loops. It is also observed that loops coalescence with increasing electron fluence to decrease its density, as an example of the coalescence and disappearance of loops shown by white arrows in Fig. 5.1 (d). Thus, e^- irradiation has been found to enhance dynamic defect recovery as shown in SiC [12]. It is also worth to note that small dot contrasts were formed at high fluence (shown by thinner white arrow in the inserted image in Fig. 5.1 (d)), although the nature of the loops are not clear at this moment.

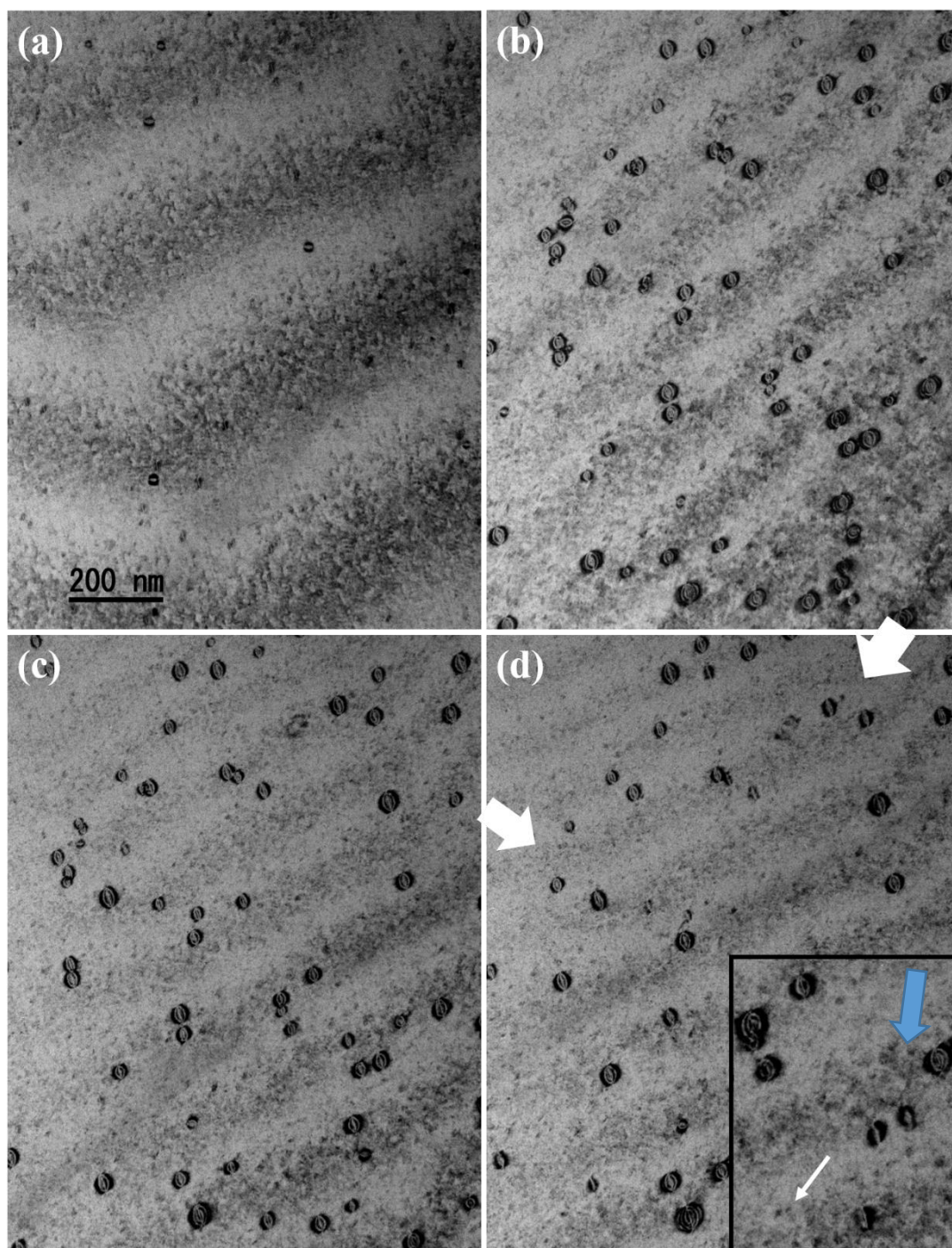


Fig. 5.1: Sequential *in situ* BF-TEM images showing the nucleation and growth of defects in xenon ion-irradiated YSZ poly-crystals irradiated with 3.0 MeV incident electron at 300 K at various dose levels: (a) $3.2 \times 10^{23} \text{ m}^{-2}$, (b) $2.9 \times 10^{24} \text{ m}^{-2}$ (c) $4.8 \times 10^{24} \text{ m}^{-2}$, (d) $8.6 \times 10^{24} \text{ m}^{-2}$. The observations were performed from the [110] direction with $g = 111$ reflection. Inserted micrograph in (d) is a magnified image of the defects formed in (d). The white arrows in (d) point to disappearance of oxygen displacement type dislocation loops and the thinner white arrow in the inserted image in (d) indicates the existence of point defects formed in the ion-tracks.

5.3.2 Irradiation at 573 K

Fig. 5.2 displays the *in situ* TEM images of the defects formed in the YSZ specimen at 573 K under 3.0 MeV electron irradiation. In contrast to the defects at 300 K, we found that only tiny dot contrasts were nucleated at this irradiation condition, which were considered to be small perfect loops. In pristine YSZ specimens (described in chapter 4) mixture of O-interstitial type and perfect dislocation loops are formed at same irradiation condition. Only small perfect dislocation loops are formed in the ion-irradiated specimen without large oxygen-type dislocation loops even at high electron fluence of $1.8 \times 10^{26} \text{ m}^{-2}$. It is also noted that the perfect dislocation loops are distributed in straight lines. The distance between those lines are around 15 nm, which approximately coincides the distance of the ion tracks (20 nm) under the assumption of the ion track formation efficiency to be unity. It is, therefore, considered that those perfect loops were nucleated along the damage region of ion tracks induced by 200 MeV xenon ions.

Fig. 5.3 shows microstructure at a thicker region of the same YSZ specimen. Initially the specimen was irradiated with broadened electron beam of $1.4 \times 10^{21} \text{ m}^{-2} \text{ s}^{-1}$ for 455 seconds and large perfect dislocation were found in the matrices (a). Focused electron beam with $3.8 \times 10^{22} \text{ m}^{-2} \text{ s}^{-1}$ caused those perfect loops to increase in size with increasing fluence and finally at $6.8 \times 10^{25} \text{ m}^{-2}$, the loops converted to dislocation lines.

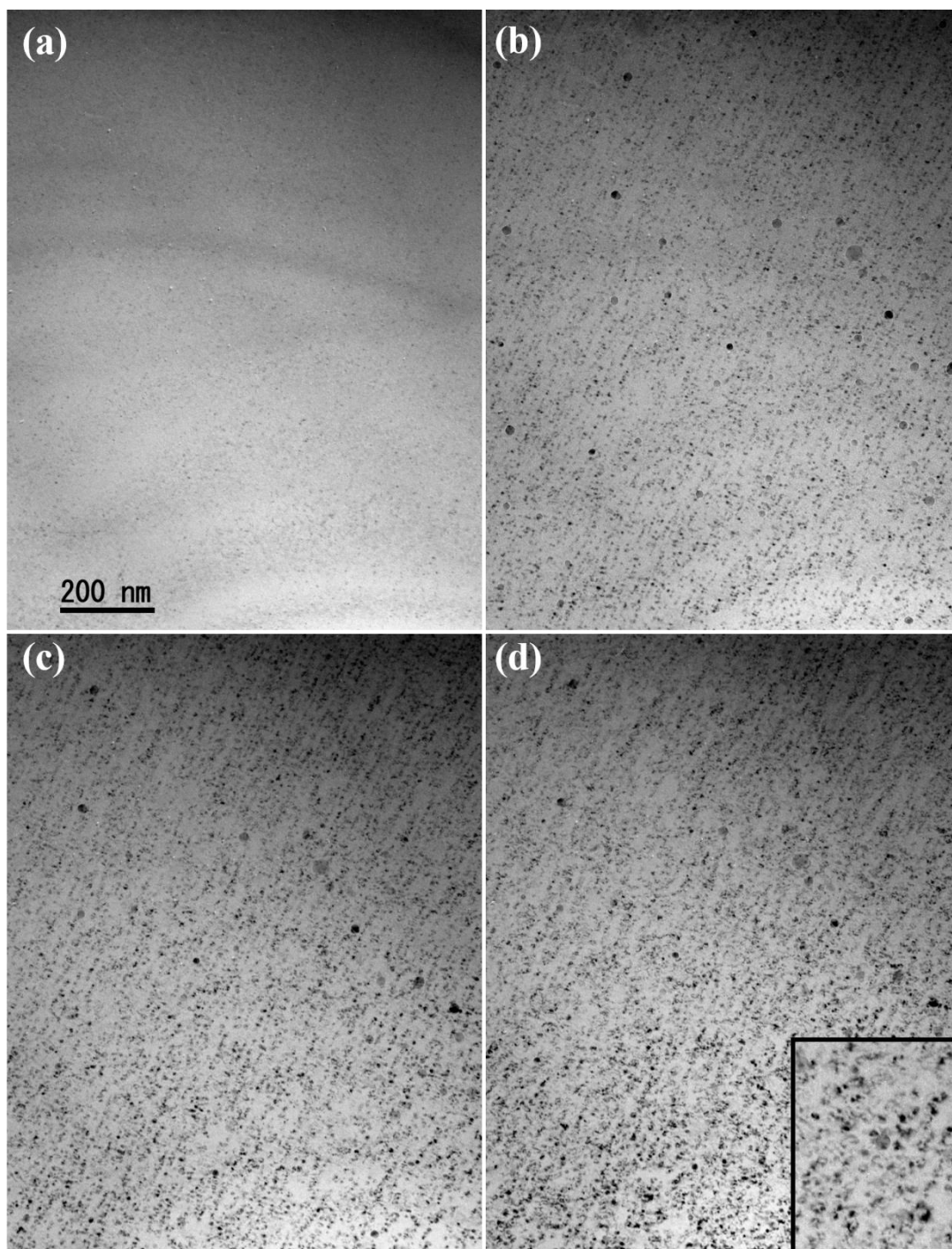


Fig. 5.2: Sequential *in situ* BF-TEM images showing the nucleation and growth of defects in xenon ion-irradiated YSZ poly-crystals irradiated with 3.0 MeV incident electron at 573 K in the thinner region of the specimen at various dose levels: (a) $6.0 \times 10^{24} \text{ m}^{-2}$, (b) $6.0 \times 10^{25} \text{ m}^{-2}$ (c) $1.2 \times 10^{26} \text{ m}^{-2}$, (d) $1.8 \times 10^{26} \text{ m}^{-2}$. The observations were performed from the [110] direction with $g = 111$ reflection. Inserted micrograph in (d) is a magnified image of the defects formed in (d).

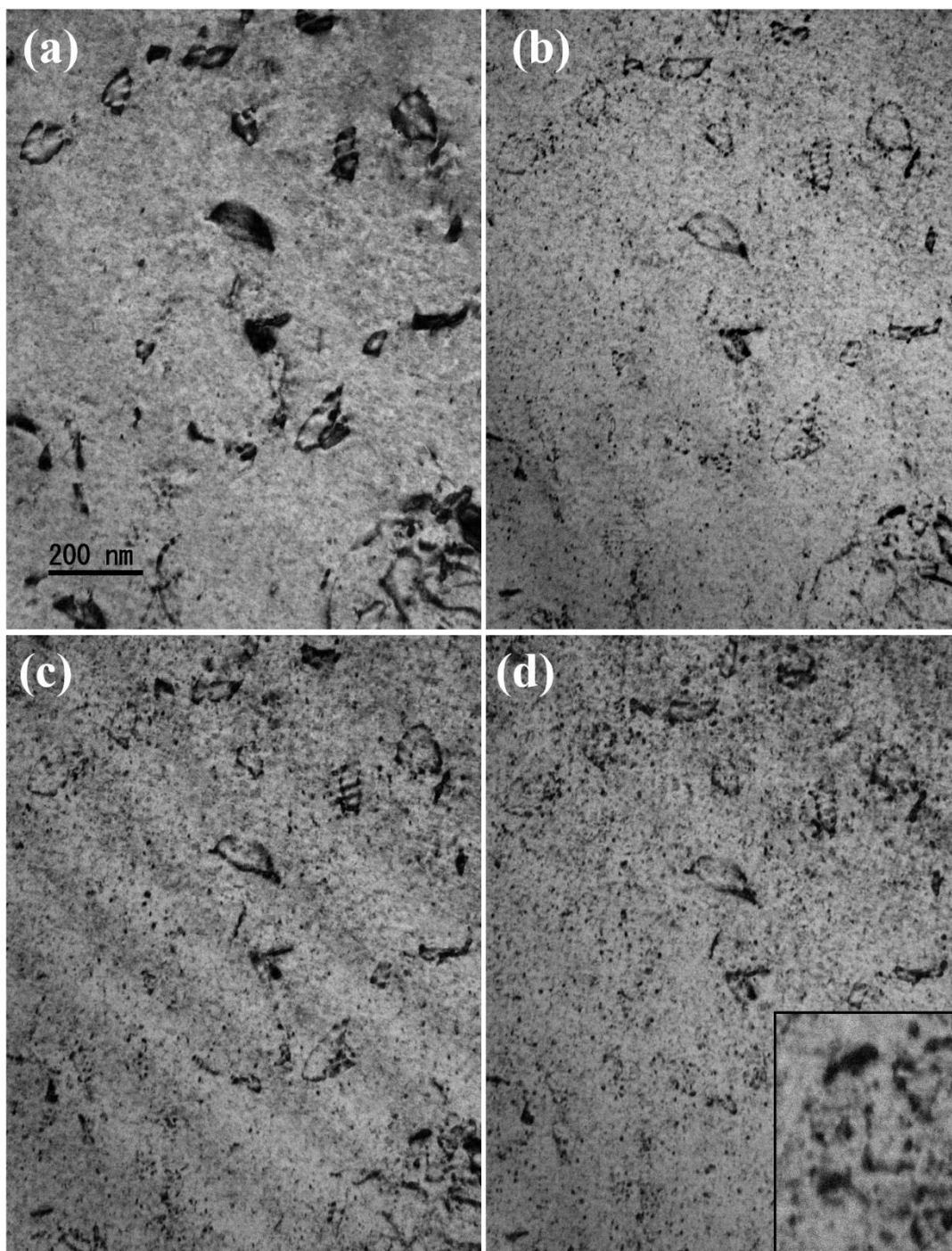


Fig. 5.3: Sequential *in situ* BF-TEM images showing the nucleation and growth of defects in xenon ion-irradiated YSZ poly-crystals irradiated with 3.0 MeV incident electron at 573 K in the thicker region of the specimen at various dose levels: (a) $4.5 \times 10^{24} \text{ m}^{-2}$, (b) $2.3 \times 10^{25} \text{ m}^{-2}$ (c) $4.5 \times 10^{25} \text{ m}^{-2}$, (d) $6.8 \times 10^{25} \text{ m}^{-2}$. The specimen was initially irradiated with a broadened beam for 455 sec with a flux of $1.4 \times 10^{21} \text{ m}^{-2}\text{s}^{-1}$. The observations were performed from the [112] direction with $g = 111$ reflection. Inserted micrograph in (d) is a magnified image of the defects formed in (d).

Higher annealing rate of defects in the thinner part of the specimen is supposed to cause the discrepancies in the defects nucleated in thinner and thicker region.

5.3.3 Irradiation at 773 K

Fig. 5.4 shows a sequential change of BF-TEM images in a thinner part of the YSZ specimen irradiated at 773 K. At 773 K, the temperature reaches the threshold value for perfect loop evolution in pristine YSZ (explained in chapter 4), and only tiny perfect dislocation loops were formed along uniformly distributed ion-tracks. In comparison to the lower irradiation temperatures (300 and 573 K), the density of small perfect loops was very high at this irradiation condition. Higher density of loops with coalescence was found in the central part of the specimen covering the electron beam area. It should be noted here that the initial electron fluence used at 773 is higher than that used in the previous cases.

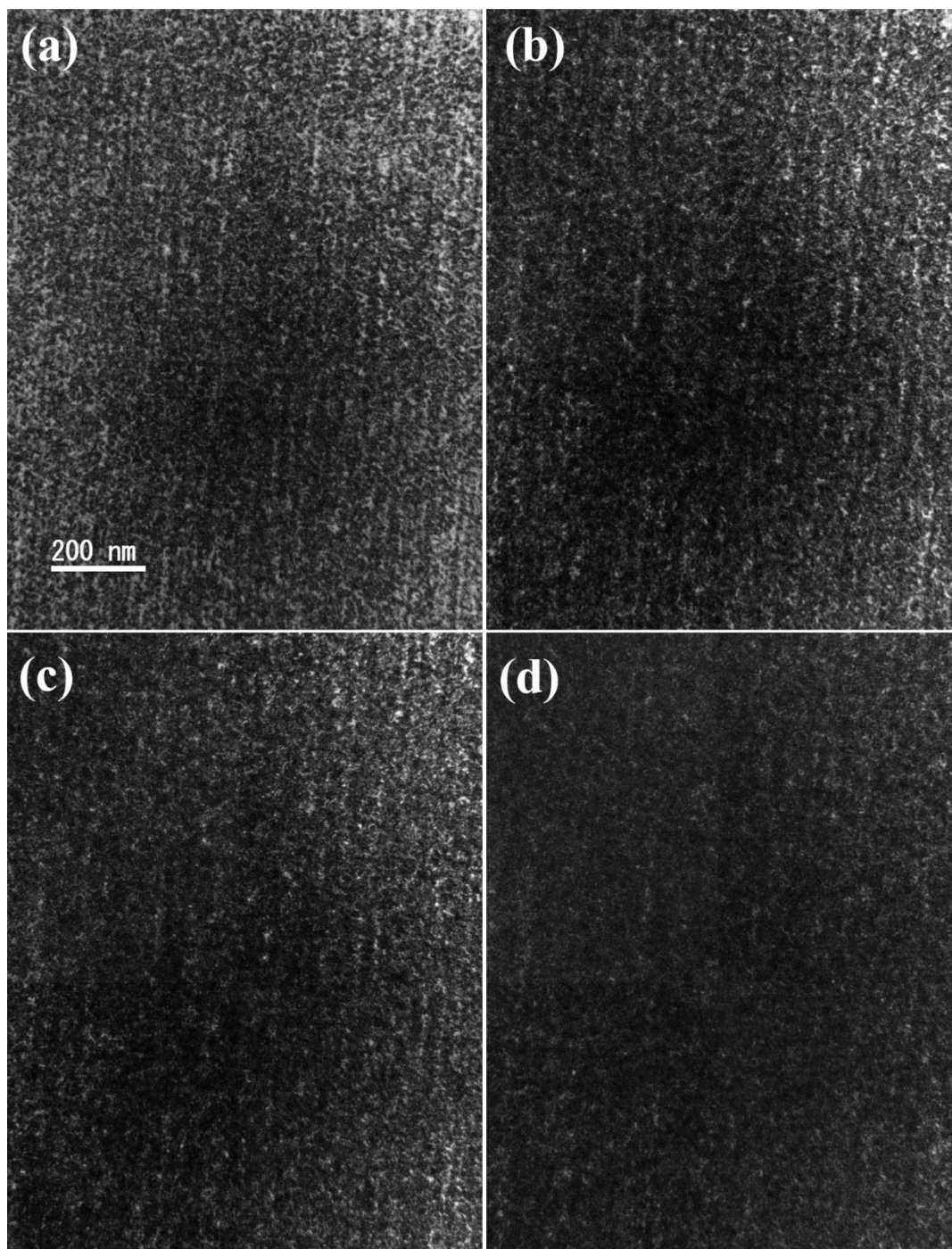


Fig. 5.4: Sequential *in situ* BF-TEM images showing the nucleation and growth of defects in xenon ion-irradiated YSZ poly-crystals irradiated with 3.0 MeV incident electron at 773 K at various dose levels: (a) $2.1 \times 10^{25} \text{ m}^{-2}$, (b) $4.3 \times 10^{25} \text{ m}^{-2}$ (c) $6.4 \times 10^{25} \text{ m}^{-2}$, (d) $1.0 \times 10^{26} \text{ m}^{-2}$. The observations were performed from the [110] direction with $g = 111$ reflection. Inserted micrograph in (d) is a magnified image of the defects formed in (d).

5.4 DISCUSSION:

Swift heavy ions loose the kinetic energy through inelastic collisions with the electrons of the constituent atoms of the target material and the resulting intense electronic excitation produces a narrow trail of damage along ion path known as ion track [13] beyond a material dependent threshold value of electronic energy loss [14, 15]. Though materials of similar crystallographic structure may have different size of ion-tracks under similar irradiation conditions [16] depending on energy density deposition, irradiation temperature, and material composition [17], its worthy to investigate the interaction of ion tracks with high energy electron irradiations.

YSZ poly-crystals irradiated with 200 MeV Xe^{14+} ions at $5 \times 10^{11} \text{ cm}^{-2}$ were subjected to 3.0 MeV electron irradiation at different irradiation temperatures to gain insights into the kinetic behavior of point defects when extended defects exist before the electron irradiation. Different nucleation behavior from the pristine specimen was observed and the microstructure was strongly dependent on irradiation temperature. The YSZ specimen is supposed to contain ion-tracks due to the high density electronic excitations along the path of incident ions [5].

At lower irradiation temperature (300 K), almost uniformly distributed oxygen displacement type dislocation loops were nucleated, whereas at higher irradiation temperatures (573 and 773 K) small perfect dislocation loops are solely

formed along the ion tracks. Since core region of ion tracks, whose size is nm order, are composed of lower atomic density (with high concentration of vacancies) [3, 13] point defects induced by high energy electrons are considered to be absorbed by the ion tracks. Oxygen interstitials with higher mobility than cation ones are accumulated at ion tracks to form larger oxygen-type dislocation loops, without forming perfect dislocation loops. Conversion to the dislocation lines was also observed at 300 K after reaching to a certain size as described in ref. [18] for 200 keV electron irradiated YSZ subsequent to 300 keV O-ion irradiation (shown by a blue arrow in the inserted image in Fig. 5.1 (d)). At high fluence, small perfect loops are formed between oxygen interstitial loops and/or ion tracks (shown by a thinner white arrow in the inserted image in Fig. 5.1 (d)). This is probably due to the accumulation of cation point defects at high fluence, since both of Zr and O sublattices are displaced at 3.0 electron irradiation. In contrast defect clusters consisting of only oxygen interstitial type loops in pristine YSZ, formation of combination of almost uniformly distributed O-interstitial loops and small perfect loops comply with the previously drawn conclusion: irradiation defects preferentially accumulate at the existing nucleation sites.

Mobility of interstitials and vacancies of O and cation sublattices increases with higher irradiation temperatures (573 and 773 K). at those temperatures, only

perfect loops were formed in YSZ specimens which were induced ion-tracks in advance (Fig. 5.2 and 5.4). The threshold irradiation temperature, at which only perfect dislocation loops are formed in the pristine YSZ, is presented in chapter 4 to be 773 K. However, for the xenon-ion irradiated YSZ specimen, the threshold temperature is decreased to 573 K. Irradiation with a broadened beam with a fluence of $6.3 \times 10^{23} \text{ m}^{-2}$ at the thicker region of the specimen also caused formation of perfect loops, although larger size of loops were formed. Further irradiation at the same region with a focused electron beam up to a fluence of $6.8 \times 10^{25} \text{ m}^{-2}$ leads to the formation of perfect loops with very small size in the matrices.

Irradiation with 3.0 MeV electrons at all irradiation temperatures used in this study shows an increasing in size of the loops, whether oxygen or perfect, with increasing fluences. Damage or disordering build-up, growth of microstructures may lead to structural modification as well, along with dynamic annealing at higher temperatures.

5.5 CONCLUSIONS:

Interaction of ion-tracks, induced by 200 MeV Xe^{14+} ion, in 8 mol% YSZ poly-crystals with 3.0 MeV electron irradiation at different irradiation temperatures has been investigated. In situ observation of dislocation loops by UHVM reveals that

the microstructure evolution and growth is quite dependent on incident electron fluence and irradiation temperatures. Higher fluences cause higher growth and coalescence rate of dislocation loops at all temperatures used in this study. On the other hand, increasing temperatures lead to the higher mobilization of interstitials of vacancies and interstitials of O and cation sublattices which eventually accelerate the defect clustering behavior. Some preliminary results of behavior of microstructure evolution, growth and aftermaths are presented here, but attempts might be taken in future for further understanding of fuel/target materials in reactor environment.

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Chapter 6

Concluding Remarks

If we have an atom that is in an excited state and so is going to emit a photon, we cannot say when it will emit the photon. It has a certain amplitude to emit the photon at any time, and we can predict only a probability; we cannot predict the future exactly.

*-Richard P. Feynman
(1918 - 1988)*

6.1 GENERAL CONCLUSIONS:

Yttria-stabilized zirconia is an important material in nuclear-based research and industry for its exceptional radiation tolerant quality even at higher irradiation temperatures. It is nowadays considered as one of the potential matrices to be used in the fuel matrix of nuclear reactors along with its usage as a target material for transmutation of actinides. As a fuel matrix, YSZ would be subjected to a variety of irradiations, e.g., alpha-beta ray, gamma radiation, x-ray, neutron irradiation and enormous kinds of fission fragments which might degrade it chemically, thermally and mechanically. So, studying the evolution of radiation damage in YSZ at extreme situations has become an important direction to work on to develop radiation tolerant materials. Accordingly, the thrust of the experimental and simulation work in this thesis has been to investigate the defect kinetics under different irradiation conditions. In this final chapter, the works done on YSZ under this thesis will be summarized and some areas that merit future research will be briefly described.

8 mol% pristine yttria-stabilized zirconia specimens were subjected to systematic series of *in situ* electron irradiation experiments in HVEMs with a range of electron energies, from 1.25 to 3.0 MeV at different irradiation temperatures (300 to 773 K) and the sequential BF-TEM images were recorded in CCD cameras. Irradiation experiments at 1.25 MeV electron energy were conducted by JEM-1300NEF (JEOL Ltd.) at the ultramicroscopy research center of Kyushu University up to an electron fluence of $\sim 4.0 \times 10^{26} \text{ m}^{-2}$, and the experiments at 1.5, 2.0, 2.5 and 3.0 MeV electron energy were carried out with an ultra-high voltage electron microscope (H-3000, Hitachi Ltd.) at Research Center for Ultra-high Voltage Electron Microscopy (UHVEM) of Osaka university up to an electron fluence of $\sim 2 \times 10^{27} \text{ m}^{-2}$. Irradiation at different temperatures ranging from 300 to 673 K showed that electron energy below 1.25 MeV does not form defect clusters due to the recombination of displaced oxygen interstitials with structural vacancies induced by doping of Y_2O_3 to compensate charge neutrality. However, two types of dislocation loops, namely perfect and/or oxygen interstitial-type ones, were formed at 1.25, 2.0, 2.5 and 3.0 MeV electron irradiations. The ratio of the displacement damage in oxygen and cation sublattices, induced by the incident electron energies was found to play an important role for the evolution of dislocation loops. The size of the loops was observed increasing with increasing electron fluences to a certain size before converting to

dislocation lines, and the focused electron beam with a Gaussian shaped intensity distribution was discussed as an influencing factor for defect migration from center of the beam to the peripheral region. A review was done on threshold displacement energy E_d , one of the most important parameters in defect evolution process, and a range of values were found for oxygen and cation sublattices in YSZ. The E_d for Zr sublattices was bracketed as $66 < E_{d, \text{Zr}} \leq 89$ eV as threshold electron energy from the formation of oxygen type loops at 1.5 MeV. Mobility of the interstitials and vacancies of oxygen and cation sublattices were found influenced by the irradiation temperatures and temperature as low as 573 K was determined as sufficient to accelerate the disordering process to nucleate perfect loops, but this threshold temperature value (573 K) was found increasing with increasing irradiation energies.

Later 8 mol% YSZ specimen was irradiated with 200 MeV Xe^{14+} ions at Tandem-Accelerator facility of Japan Atomic Energy Agency-Tokai up to a fluence of $5 \times 10^{11} \text{ cm}^{-2}$, prior to irradiation with 3.0 MeV electrons in a HVEM at different temperatures from 300 to 773 K. These experiments are performed to simulate interactions among defects induced by various kinds of radiation in actual nuclear environment. Electron irradiation at 300 K produced uniformly distributed oxygen interstitial type loops, which are considered to be nucleated at the ion tracks, with a trend to increase in size with increasing fluence up to a certain size before coalescence

with neighboring one to form bigger loops. Further irradiation at higher temperatures at 573 and 773K showed formation of only perfect-type dislocation loops with a very high density along the ion-tracks. Higher irradiation temperature accelerated the formation of perfect loops, which is attributed to the higher mobility of the interstitials and vacancies of constituents of the materials.. In contrast to the pristine YSZ, threshold temperature to produce perfect loops descended to a lower value for 3.0 MeV electron irradiation.

Based on the *in situ* electron irradiation experiments with 8 mol% pristine and ion-irradiated YSZ with 200 MeV Xe ions described above, the contributions of this dissertation are summarized as follows:

- The ratio of the displacement damage in cation and O sublattices in YSZ, induced by the incident electron energies was found to be a principal factor for controlling the evolution of dislocation loops.
- The threshold electron energy for evolution of defect clusters has been determined to be 1.5 MeV. The threshold displacement energy values of anion and cation sublattices are discussed based on the energy dependent microstructure: the threshold displacement energy for Zr sublattices in YSZ has been bracketed as $66 < E_{d,Zr} \leq 89$ in eV.
- Types of loops, namely perfect and/or oxygen interstitial type, under high

energy electron irradiation has been distinguished based on previous reports and $g \cdot b$ analysis.

- The intensity distribution of electron flux in a typical electron beam used for this research work has been found influencing the migration of oxygen interstitials from center to the peripheral region of the beam, which cause the formation of oxygen-type dislocation loops at the region where the concentration gradient of interstitials is maximum..
- Role of irradiation temperatures for nucleation-growth-stabilization-recovery process of defects, such as dislocation loops, has been discussed. Threshold irradiation temperatures for evolution of only perfect loops are found to be 573, 673 and 773 K for 1.5, 2.5 and 3.0 MeV electron irradiations, respectively.
- Preliminary results on interaction of different types of defects in YSZ has been presented for 3.0 MeV electron irradiation subsequent to swift heavy ion irradiation.

6.2 DIRECTIONS FOR FUTURE RESEARCH:

Despite years of application of YSZ as a surrogate material to understand the microscopic insights of the nuclear fuel, the mechanism of displacement damage

accumulation of defect clusters is not fully understood. The experimental and simulation works conducted during the course of this dissertation have served to enhance the understanding of the effect of electron energy and irradiation temperatures for the evolution of dislocation loops. However, there remain quite a few challenges down the road before getting a radiation resistant material to use in practically harsh radiation environment. This work briefly tribute to the interaction of selective displacement damage with existing ion-tracks in the matrices, but further systematic TEM investigation is necessary to unfold the actual scenario with varying electron energies and irradiation temperatures.

Scanning transmission electron microscopy (STEM) techniques including high-angle annular dark-field (HAADF) and annular bright-field (ABF) imaging could be applied to clarify the structure of ion-tracks in YSZ prior to high energy electron irradiation. The atomic scale analysis of ion tracks in YSZ is believed to give useful information on the interaction between ion tracks and isolated defects induced by electron irradiation. It is also emphasized that further systematic investigations with different energies and temperatures are necessary. Comprehensive studies with other advanced experimental characterization techniques, such as Rutherford backscattering spectrometry and channeling (RBS/C) and x-ray diffraction (XRD) with different sensitivities to the radiation damage along with MD simulation could

be employed to probe the structural transformations induced in cubic YSZ under different irradiation conditions.