8. Summary and Conclusions

8.1 Summary and Conclusions

This chapter summarizes all points of the present thesis work and it includes a brief discussion of the introduction, significant results, conclusions, and future perspectives.

Nuclear power generation is one of the most important and useful applications of nuclear reactors as it can moderately substitute fossil fuels. However, a variety of radioactive nuclear wastes are generated at the diverse phase of nuclear fuel processing. Therefore, there is a necessity for safe and effective management of these hazardous and environmentally sensitive radioactive wastes.

Ceramic materials based on different compositions have been examined against the immobilization of radionuclide waste and actinides transmutations.

Among the ceramic crystalline compounds, the pyrochlore oxides have been considered a promising candidate for the immobilization of radioactive nuclear waste. However, the biggest challenge of designing and fabrication of complex pyrochlore oxides with the engineering of crystal structures from pyrochlore to defect fluorite is still open. Processing and synthesis of ceramic and other materials should be designed with specific attention to controlling and changing the chemical and physical properties for promising use in modern era emerging applications.

In the present investigation, a series of zirconate pyrochlore oxides, i.e., $La_2Zr_2O_7$ and $Gd_2Zr_2O_7$ samples were prepared *via* a standard solid-state method, and the impact of extremal parameters, i.e., annealing temperature, irradiation temperature, ion energy, and ion fluence on the structural modification were explored. To investigate the impact of annealing temperature and time, the $La_2Zr_2O_7$ samples were annealed at different temperatures and times.

To compute the impact of irradiation temperature and ion fluence on the structural modifications of $La_2Zr_2O_7$ samples were irradiated with 1.00 MeV Xe^{4+} and 500 keV Kr^{2+} ions. Further, the radiation tolerance of $Gd_2Zr_2O_7$ samples with the function of different degrees of structural ordering/disordering and ion fluence upon irradiation of swift heavy ion irradiation (100 MeV, I^{7+} ions) were explored. To evaluate the annealing/sintering temperature and ion irradiation induced structural modifications the different complementary analytical characterization techniques such as XRD, GIXRD, FE-SEM, Raman spectroscopy, and HR-TEM were employed.

Structural and microstructural properties of $La_2Zr_2O_7$ samples transformed with the augmentation of the annealing temperature and extended time duration. The XRD analysis demonstrates the enhancement in the crystallinity of the $La_2Zr_2O_7$ samples with enrichment of annealing temperature and extended time duration. The Rietveld refinement of the $La_2Zr_2O_7$ samples confirmed the formation of cubic structure pyrochlore phase. The qualitative evaluation of variable oxygen parameter 'x_{48f}' and cation ordering revealed the enrichment of the pyrochlore phase structure. FE-SEM results strengthen the XRD studies and established grain growth evolution of $La_2Zr_2O_7$ samples. The grain growth component revealed that the curvature-driven migration/diffusion of grain boundaries occurred at elevated temperatures for a prolonged duration. An outcome of the investigation divulges that the preselected and destined parameters were found to be capable of tailoring the microstructure and structural ordering that enchant the research community because having tremendous applications in diverse fields.

$La_2Zr_2O_7$ samples irradiated in a well-controlled environment using 1.0 MeV Xe^{4+} ions with the function of ion fluence at two different temperatures (88 K and 300 K) demonstrate the splendid structural response. The microstructural study of the un-irradiated $La_2Zr_2O_7$ sample exhibits that the grains and grain boundaries are evidently noticeable. The GIXRD studies exhibit the deterioration of the crystallinity of $La_2Zr_2O_7$ samples. The deterioration of the crystallinity enhanced monotonically with augmentation of fluence at both the temperatures. Rietveld refinement indicates that the lattice parameters of $La_2Zr_2O_7$ samples enhanced with the augmentation of ion fluence. We wish to stress that as per the earlier studies defects are immovable at low temperature whereas defects become mobile at room temperature. The relatively higher deterioration of the crystallinity at 88 K in comparison of 300 K may be correlated with the immobility nature of defects at ~ 88 K. Fig. 8.1 illustrates the impact of irradiation temperature and ion fluence on the degradation of crystallinity (damage) of $La_2Zr_2O_7$ samples. Raman spectroscopy analysis suggests the concurrently weakening and broadening of the vibrational modes of $La_2Zr_2O_7$ samples upon irradiation and are relatively higher at ~88 K. Both, GIXRD and Raman spectroscopy indicated that the damage is more pronounced at ~ 88 K with the increment of ion fluence. The HR-TEM micrographs of $La_2Zr_2O_7$ samples confirmed that the deterioration of atomic ordering is more pronounced at ~88 K than 300 K.

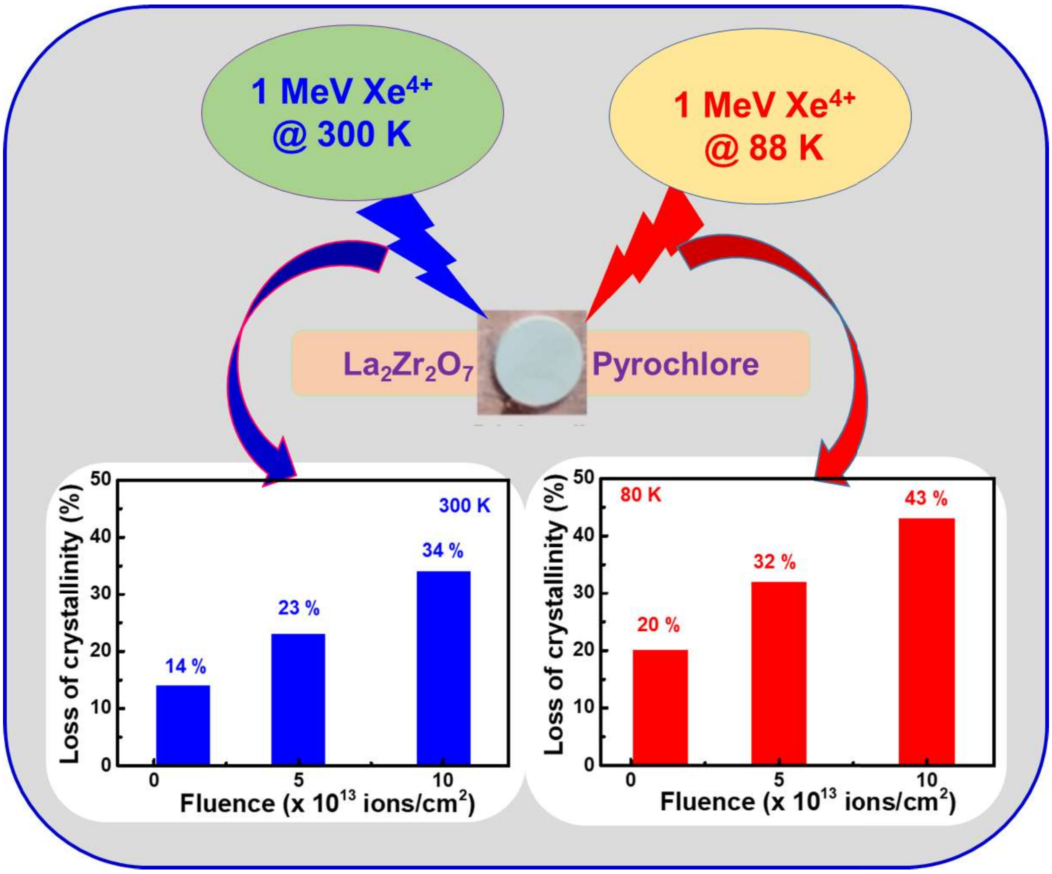

Figure 8.1 *Illustrates the impact of irradiation temperature and ion fluence on the degradation of crystallinity (damage) of $La_2Zr_2O_7$ samples.*

The influence of low-energy ion irradiation (500 keV, Kr^{2+}) on the structural response of $La_2Zr_2O_7$ samples was investigated with the function of irradiation temperature (88 K and 300 K) and ion fluence. The before and after irradiation of $La_2Zr_2O_7$ samples were studied using GIXRD and Raman spectroscopy techniques. Upon irradiation concurrently weakening and broadening of $La_2Zr_2O_7$ superstructure reflections enhanced with the augmentation of ion fluence at both the temperatures (88 K and 300 K), i.e., the ion irradiation induced structural disordering. The prudent evaluation of superstructure reflections of $La_2Zr_2O_7$ samples shows that the reduction in the intensity of superstructure reflections is relatively pronounced at ~88 K than 300 K [Fig. 8.2], which indicates that at a lower temperature (~88 K), the deterioration of the periodic ordering of crystal structure is comparatively prominent. It is observed that at both the temperatures, the $La_2Zr_2O_7$ reflections shift to lower 2θ with the enhancement of fluence. The shifting of reflections towards lower 2θ specifies the engineering of lattice swelling with the function of fluence and irradiation temperature. Moreover, the lattice strain and cell volume expansion depend on the irradiation temperature and fluence; are significantly more pronounced at 88 K than 300 K. Figure 8.2 demonstrates the variation of superlattice reflections, cell volume, cation disorder, and '*x*' parameter of 48f oxygen with function on ion fluence.

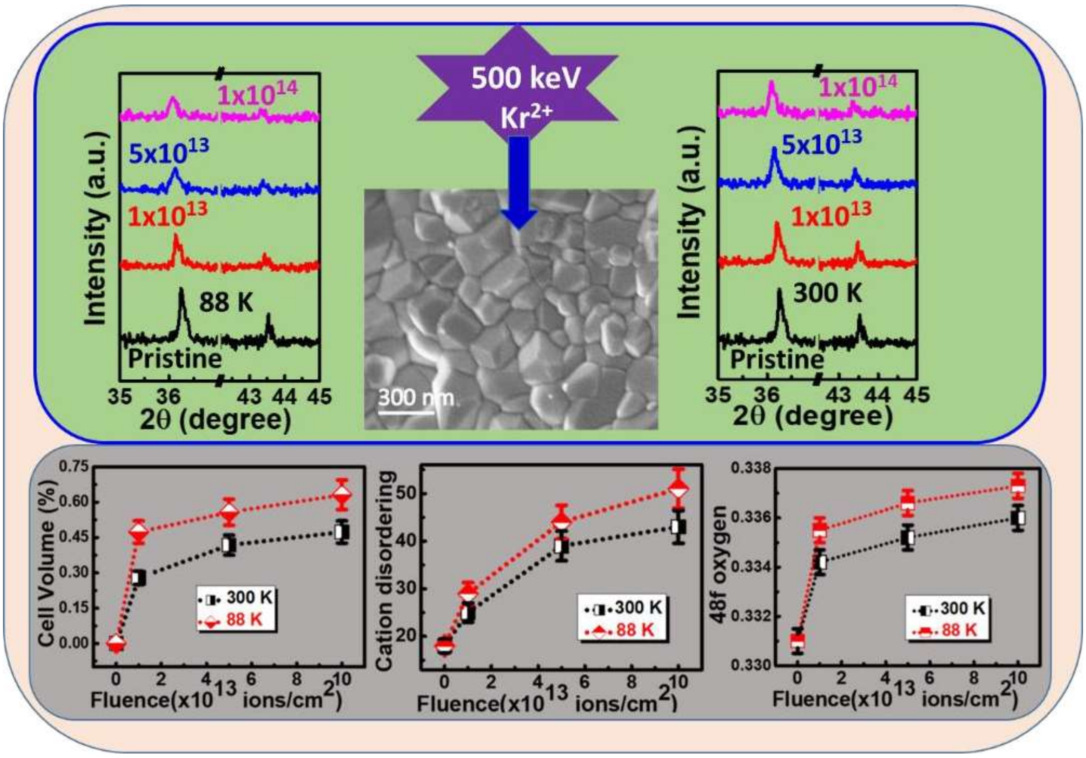

Figure 8.2 *Variation of superlattice reflections, cell volume, cation disorder, and 'x' parameter of 48f oxygen with function on ion fluence.*

Cation disordering enhances as a function of ion fluence and it is relatively higher at 88 K. The oxygen positional parameter, x_{48f}, determines the deviation of crystal structure in pyrochlore oxides indicates that the value of the x_{48f} parameter is also enhanced with the enrichment of ion fluence. It is found to be higher at 88 K than 300 K for similar fluence. The relatively higher value of the x_{48f} parameter at 88 K also signifies pronounced disordering/defects at low temperature. We wish to stress that the post-irradiation Raman spectra do not exhibit anomalous variation except relative reduction in the intensity and augmentation in the FWHM. The Raman modes significantly became broadened and weakened with the augmentation of fluence from 1.0×10^{13} to 1.0×10^{14} ions/cm^2. Further, Raman spectroscopy analysis confirmed the higher disorder/distortion in the system at 88 K in comparison of 300 K. Both, the XRD and Raman spectroscopy confirmed more pronounced structural modification (defects/disordering) in $La_2Zr_2O_7$ samples at 88 K in comparison of 300 K due to the immobile nature of ion irradiation-induced disorder/defects.

The impact of structural ordering/disordering on the radiation tolerance of $Gd_2Zr_2O_7$ samples sintered at 1500°C (GZO15) and 1400°C (GZO14) has been investigated using XRD, FE-SEM, and Raman spectroscopy. Peak fitting profile analysis and Rietveld refinement of GZO14 and GZO15 samples demonstrate that both samples possess some different degrees of pyrochlore super-structural ordering. Raman spectroscopy studies also confirm the existence of the pyrochlore phase in both GZO samples and strengthen the Rietveld analysis. The different degrees of pyrochlore phase GZO14 and GZO15 samples were irradiated using 100 MeV I^{7+} ions at the fluence of 1.0×10^{14} ions/cm^2. Raman studies illustrate the presence of weak pyrochlore phase ordering while XRD analysis exhibited pyrochlore to fluorite phase transition upon irradiation. Both, the XRD and Raman spectroscopy studies exhibited that the GZO15 sample displays better radiation tolerance than the GZO14 sample. The better radiation tolerance of the GZO15 sample seems associated with some extent of the ordered pyrochlore phase. The results reported here are appreciable as they may pave a path for the fabrication of complex oxide materials with different degrees of ordering/disordering for better radiation tolerance. Assessment of radiation resistance of $Gd_2Zr_2O_7$ samples establishes the feasibility of it for the possible applications in hostile environments such as radiation tolerant hosts for safe and effective management of radioactive nuclear wastes and surplus actinides.

Further, $Gd_2Zr_2O_7$ samples were irradiated using 100 MeV I^{7+} ions and the impact of ion fluence on the structural modifications for possible use in nuclear applications was explored. XRD and Raman spectroscopy were employed to examine the radiation-induced structural modifications (O-D transformation). The Rietveld refinement of the pristine $Gd_2Zr_2O_7$ samples exhibited the ordered pyrochlore structure. XRD analysis confirmed the irradiation induced structural modifications, i.e.., pyrochlore to defect fluorite phase transition in $Gd_2Zr_2O_7$ samples, and found to be ion fluence dependent. Specifically, the $Gd_2Zr_2O_7$ samples irradiated for initial fluences (1.0×10^{12} ions/cm^2 and 3.0×10^{12} ions/cm^2) present the least degree of phase fraction. The Raman spectroscopy analysis also confirms the order-disorder in $Gd_2Zr_2O_7$ samples. The degree of the disorder is enhanced as a function of ion fluence and disregards the appearance of amorphization. The pyrochlore to defect fluorite phase transformation without any signature of amorphization, even for the highest fluence, establishes the potentiality of GZO samples for utilization in nuclear applications as radioactive waste forms.