PREFACE

Nuclear energy emits extremely little carbon and other pollutants, and it currently produces 11% of the world's electricity. However, the different types of radioactive nuclear wastes are generated at the different stages of nuclear fuel processing in the nuclear power plant. Therefore, the safe and effective management of radioactive wastes is of utmost importance. Materials used for effective management of (involving their safe discharge and storage) radioactive wastes should be stable in radioactive environments. The designing and fabrication of radiation-resistant compounds for the immobilization of radioactive wastes are of supreme importance. The scientific community is looking for appropriate materials for the safe disposal and management of radioactive wastes all over the world.

The borosilicate glasses are enormously used as a host matrix for the immobilization of high-level radioactive nuclides. However, the metastable nature of the material is a major concern for such types of matrices. Moreover, under an accidental scenario, ingression of water into glass matrices can cause the development of water-soluble salts and results in, enrich the propensity of leachability of certain immobilized constituents. Based on the requirements, there are several forms of crystalline ceramics phase which have been utilized for radioactive waste immobilization. Ceramic matrices have numerous advantages such as lower leaching rate, high radiation tolerance, high chemical, and thermal stability which are inevitable parameters for the immobilization of radioactive nuclides.

Among the several ceramics, the pyrochlore compounds have been reflected as a potential candidate for the safe and effective management of radioactive nuclides because of having complex crystal structures that ease the accommodation of diverse actinides at different crystallographic sites. The ion irradiation-induced amorphization and phase transformation from ordered pyrochlore to defect fluorite structure (O-D transformation) strongly depend on their chemical composition, irradiation temperature, ion energy, fluence, *etc*.

In this dissertation, we present a comprehensive approach for alteration of structural modifications of $La_2Zr_2O_7$ and $Gd_2Zr_2O_7$ upon annealing temperature and ion irradiation for possible application in hostile environments and other several emerging applications for societal development. 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 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.

The present thesis is categorized into eight chapters, the chapters related to integrated results with respective discussions (i.e. Chapter 3 to Chapter 7) confined between the introduction (Chapter 1) followed by synthesis process and experimental techniques (Chapter 2) and a conclusion chapter (Chapter 8).

Chapter 1 deals with the general information of nuclear wastes generated during the operation of the nuclear power plant, types of different crystalline ceramics, classification of pyrochlore oxides, zirconate pyrochlores, and use of pyrochlore oxides particularly zirconate pyrochlores in different technological applications. The motivation, objective, and scope of the thesis are also described in chapter 1.

Chapter 2 describes the comprehensive information of materials, synthesis method (preparation of $La_2Zr_2O_7$ and $Gd_2Zr_2O_7$), and irradiation experiments. The brief discussion of experimental techniques (e.g., XRD, FE-SEM, GIXRD, Raman spectroscopy, HR-TEM, *etc.*) which were employed to investigate the $La_2Zr_2O_7$ and $Gd_2Zr_2O_7$ samples are also discussed in chapter 2.

Chapter 3 discusses the influence of annealing temperature and time on the structural and microstructural properties of $La_2Zr_2O_7$. The structural and microstructural properties of $La_2Zr_2O_7$ altered with an increase of annealing temperature and extension of annealing duration. The grain growth process is governed by the curvature-driven diffusion/migration of grain boundaries. The existence of pyrochlore phase ordering at high temperature (1500°C) establishes the capabilities of $La_2Zr_2O_7$ for high-temperature applications.

Chapter 4 elucidates the structural response of $La_2Zr_2O_7$ upon ion irradiation of 1.0 MeV Xe^{4+} ions at two different temperatures (88 K and 300 K) with an increase of ion fluence (1.0×10^{13}, 5.0×10^{13}, 1.0×10^{14} ions/cm^2). The deterioration of crystallinity (damage) in the $La_2Zr_2O_7$ system was quantified from GIXRD, Raman spectroscopy, and HR-TEM studies.

Chapter 5 explains the impact of low energy ion irradiation (500 keV, Kr^{2+}) on the $La_2Zr_2O_7$ system with the function ion fluence at 88 K and 300 K. GIXRD and Raman spectroscopy analysis demonstrate the engineering of structural properties. The degree of disordering enhances with the increase of fluence and shows relatively higher disordering at a lower temperature (88 K).

Chapter 6 investigates the radiation resistance stability of $Gd_2Zr_2O_7$ samples. 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. 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 to compute the impact of some extent of the ordered pyrochlore phase.

Chapter 7 delineates the order-disorder transition, i.e., pyrochlore phase to disordered fluorite structure. In this chapter, the radiation response of $Gd_2Zr_2O_7$ upon irradiation of 100 MeV iodine ion with the fluence of 1.0×10^{12}, 3.0×10^{12}, 1.0×10^{13}, 3.0×10^{13}, and 1.0×10^{14} ions/cm^2 were investigated. Both, powder XRD and Raman spectroscopy provide the compatible elucidation of structural modifications (phase transformation) upon irradiation of swift heavy ions (100 MeV iodine).

Chapter 8 summarizes the overall concluding remarks drawn from the thesis. This chapter also highlights the feasible scope of outspreading this work in the near future.