Abstract

Continuous increase in population and thereby increase in the demand for energy from all over the world is attracting the scientific community towards the search for a clean and reliable energy source. Nuclear energy can be a great solution as the proponents mark it as a clean, reliable, and sustainable energy source with reduced carbon emissions; and hence it can make a significant contribution to global energy needs. Nuclear power generation is one of the most important and useful applications of nuclear reactors as it can moderately substitute fossil fuels. But, "If the spread of nuclear energy cannot be decoupled from the spread of nuclear weapons, it should be phased out". However, keeping the positive side onsight; researchers are trying to solve the concerns related to nuclear energy production. One of them is radioactive waste; by-products of the nuclear fuel cycle (NFC). The NFC operations involve the operation of the reactor, recycling of spent fuel, and fabrication of fuel, and producing nuclear waste which includes high, intermediate, and low-level radioactive waste (HLW, ILW, and LLW). Not only NFCs but also the nuclear power generation and other nuclear-related applications, for example, fusion and fission industry, defence programs, research, and agriculture produce nuclear radioactive waste as a by-product. To assure the tenable application of nuclear energy, it is pivotal to manage nuclear waste, especially HLW, securely and cogently. The HLW should be immobilized to ensure its safety for storage, transportation, and final repository disposal**.** The challenges that are considered for selecting a waste form include, but are not limited to (i) ability to upload large radioactive waste, (ii) easy production of the system, (iii) high radiation stability under environmental conditions, (iv) possible upload of the mixture of radioactive nuclides and other pollutant species resulting in minimal secondary phases creation, (v) must be agreeable with 'near field environment' of the waste geological repository, *etc*.

Ceramic materials based on different compositions have been examined against the immobilization of radionuclide waste and actinides transmutations. Based on the requirements, there are several forms of crystalline ceramics phase which have been utilized for radioactive waste immobilization. Among the ceramic crystalline compounds, the pyrochlore oxides have been considered a promising candidate for the immobilization of radioactive nuclear waste.

In the present investigation, we have prepared the zirconate pyrochlore oxides, namely, $La_2Zr_2O_7$ and $Gd_2Zr_2O_7$ *via* a standard solid-state method. Firstly, the $La_2Zr_2O_7$ samples were annealed at three different temperatures (1200, 1300, and 1500°C) and time (24, 48, and 96 h), to investigate the impact of annealing temperature and time on the structural and microstructural properties. Secondly, the $La_2Zr_2O_7$ samples were subjected to lighter ion Xe^{4+}

and Kr^{2+} ion irradiation at two different temperatures (88 K and 300 K), to explore and elucidate the light energy ions induced structural transformations as a function of irradiation temperature and ion fluence. Lastly, the $Gd_2Zr_2O_7$ were subjected to swift heavy (100 MeV) I^{7+} ions irradiation to investigate the radiation tolerance as a function of different degrees of structural ordering and ion fluence for possible use in nuclear applications. The pristine and post irradiated $La_2Zr_2O_7$ and $Gd_2Zr_2O_7$ were analyzed by XRD, GIXRD, FE-SEM, Raman spectroscopy, and HR-TEM. Consequently, structural and microstructural properties of $La_2Zr_2O_7$ and $Gd_2Zr_2O_7$ systems as a function of annealing time, irradiation temperature, ion energy, and ion fluence were investigated. To achieve the objective of the present research work, the thesis is divided into eight chapters, and the content of each chapter is as follows.

Chapter-1 includes a brief discussion of different types of radioactive waste and actinides and an overview of the challenges that should be considered for selecting waste forms. The distinctive crystalline ceramic host matrices are explored for radioactive waste immobilization. A comprehensive review on how external parameters, i.e., chemical substitution, annealing temperature, pressure, irradiation temperature, and ion energy modified the structural properties of pyrochlore oxides have also been discussed. The features of pyrochlore oxides that make them different from other ceramic oxides are also explained. Chapter-2 describes the synthesis method, irradiation process, and different characterization techniques used for analyzing the $La_2Zr_2O_7$ and $Gd_2Zr_2O_7$ samples. The evaluation of structural and microstructural properties of $La_2Zr_2O_7$ with the enhancement of annealing temperature and time is discussed in chapter-3. The ion irradiation, 1.0 MeV Xe^{4+}, and 500 keV Kr^{2+}, induced structural modifications with the function of irradiation temperature (i.e., 88 K and 300 K) and ion fluence are discussed successively in chapter-4 and chapter-5. The radiation tolerance capability of $Gd_2Zr_2O_7$ samples with the function of structural ordering and ion fluence for the possible applications in hostiles environments, i.e., the safe and effective management of high-level radioactive waste and actinides is discussed in chapter-6 and chapter-7. Chapter-8 delineates summarizes the overall concluding remarks drawn from the thesis by justifying its title and proposed objectives. This chapter also highlights the probable scope of outspreading this work in the near future.