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संत लौंगोवाल अभियांत्रिकी एवं प्रौद्योगिकी संस्थान
(भारत सरकार द्वारा स्थापित)
Sant Longowal Institute of Engineering & Technology
DEEMED UNIVERSITY (Established by Govt. of India)

Micro-structural analysis & radiation stability studies in undoped and cerium doped zirconolite

by

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Nuclear Waste

- A wide variety of wastes is released from nuclear and medical industries. But nuclear wastes released during the power generation are more harmful due to the presence of highly radioactive atoms e.g. U, Pu, ^{237}Np, ^{241}Am, ^{244}Cm, ^{129}I etc.
- Nuclear wastes are hazardous to all lives and environment. So these wastes must be separated from environment.
- Classification of nuclear wastes:

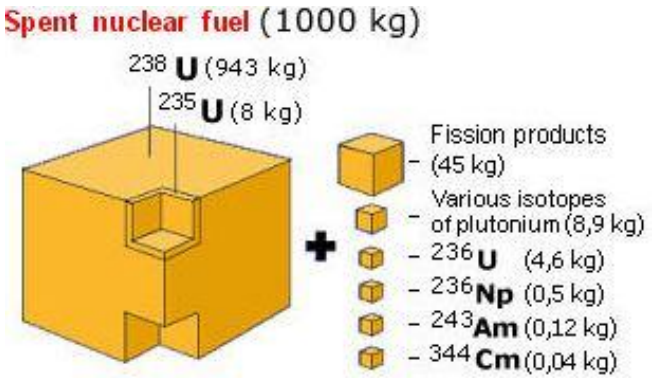
WASTES	VOLUME	HALF LIFE TIME	RADIOACTIVE CONTENT
Low Level Waste	**90%**	**Very Short Lived < 100 Days**	**1%**
Intermediate Level Waste	**7%**	**Short Lived < 30 Years**	**4%**
High Level Waste	**3%**	**Long Lived > 30 Years**	**95%**

Challenge!!!!!

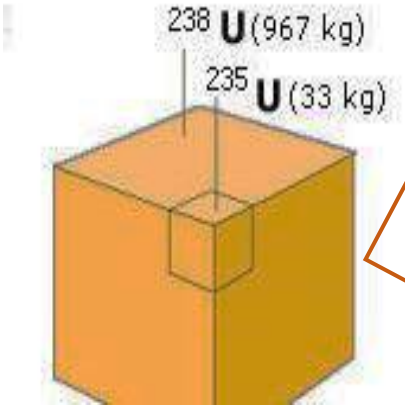
How to immobilize the high level wastes???

High level wastes(HLWs)

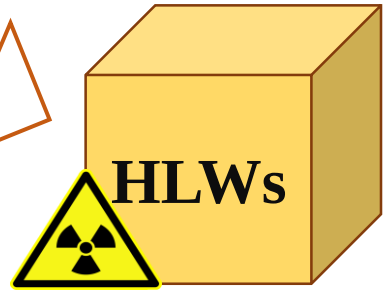
Burning of fuel



Reprocessing

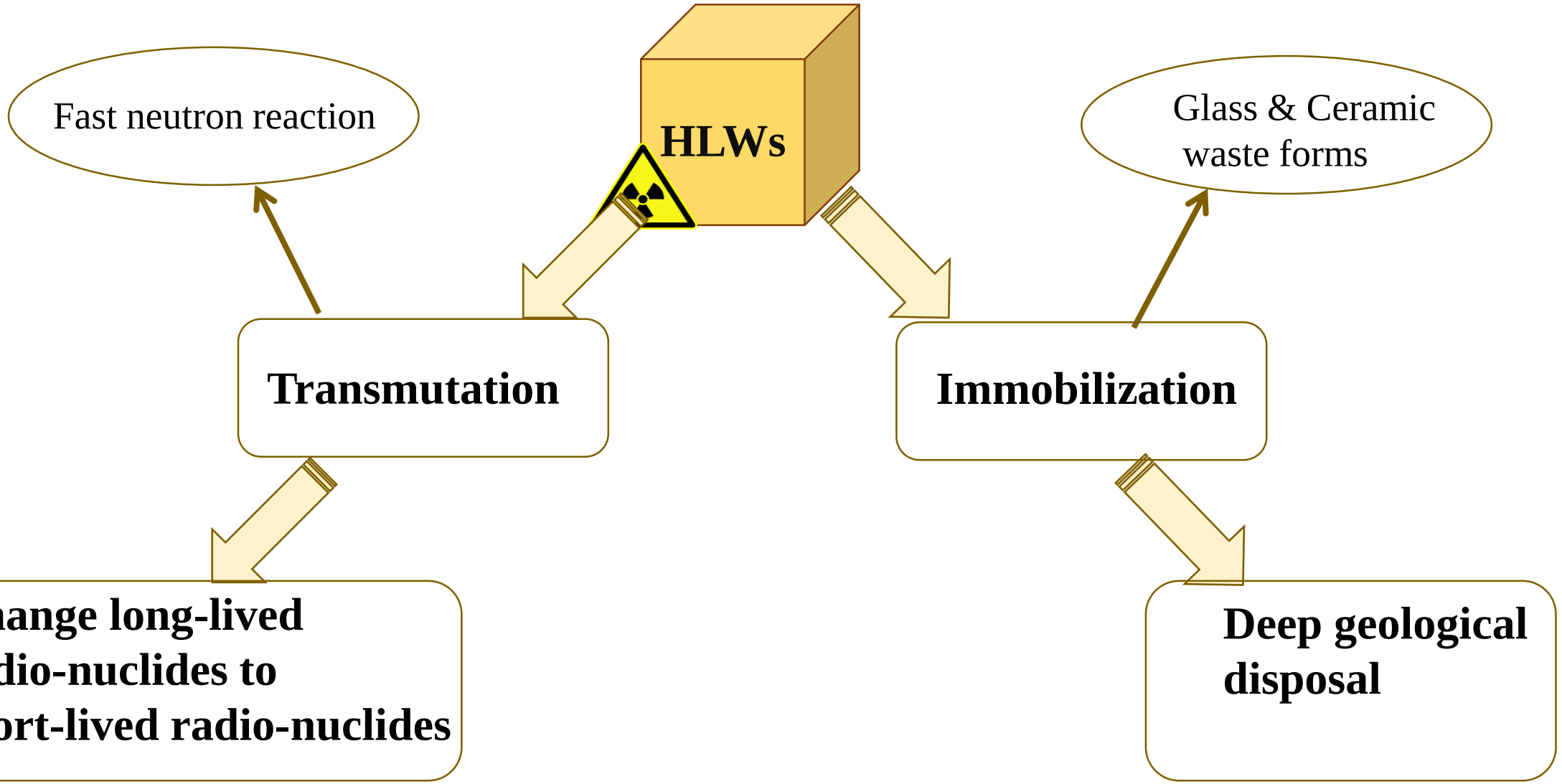


Extracted U & Pu



http://www.energyweb.cz/web/rao/eng/11.htm

Nuclear Waste Management



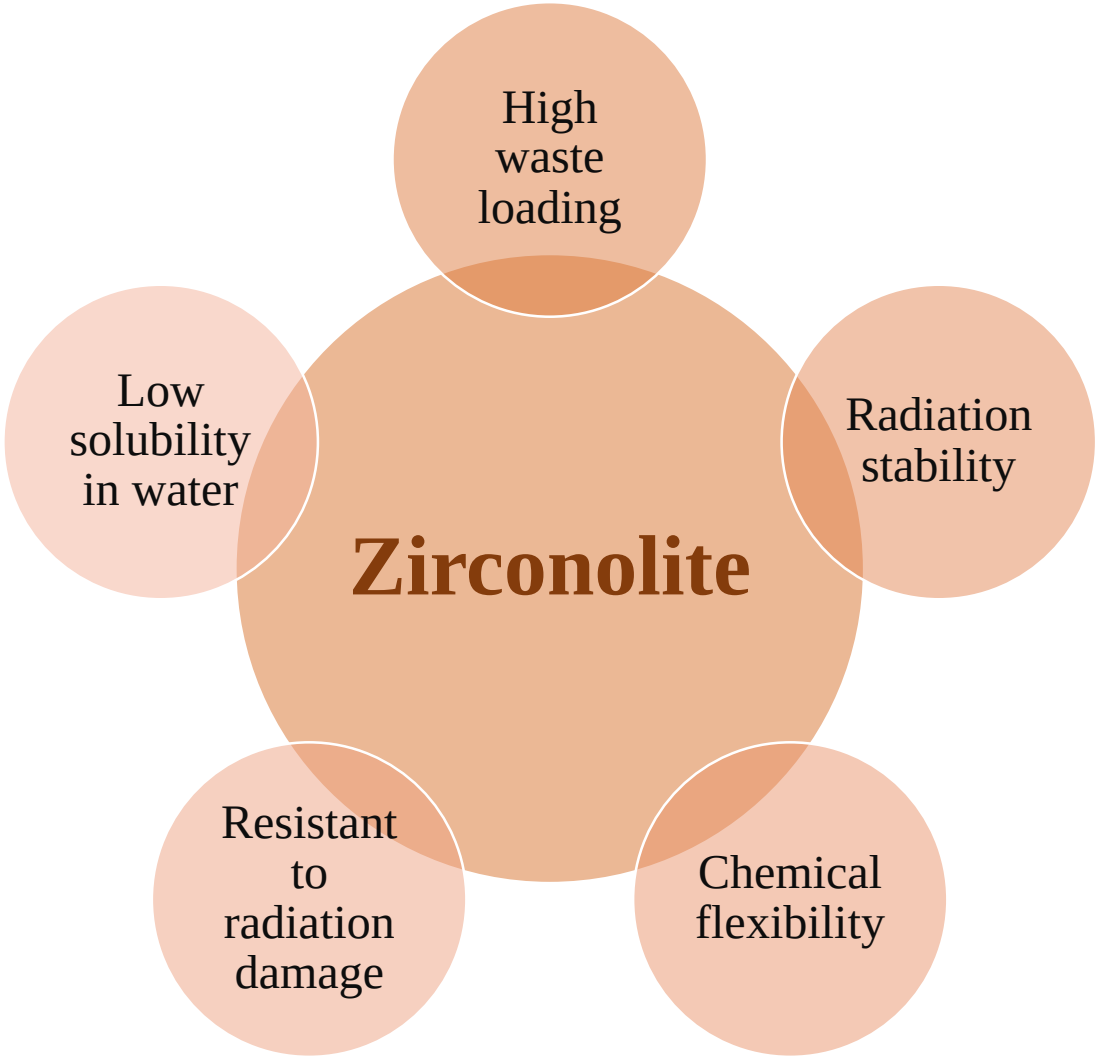
Potential waste forms

Glass waste form

- **Borosilicate glasses**
- **Phosphate glasses**

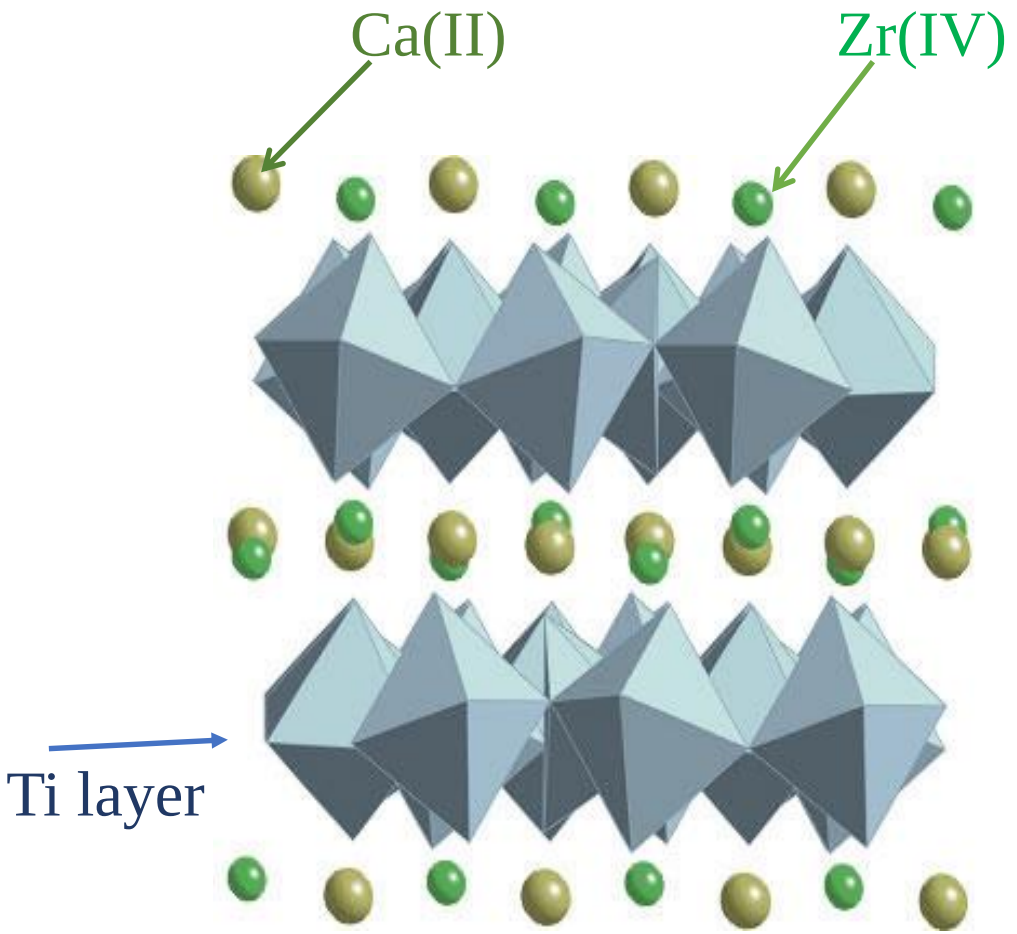
Ceramic waste form

- **Perovskite ($CaTiO_3$)**
- **Pyrochlore ($A_2B_2O_7$)**
- **Zirconolite ($CaZrTi_2O_7$)**
- **Hollandite ($BaTi_8O_{16}$)**



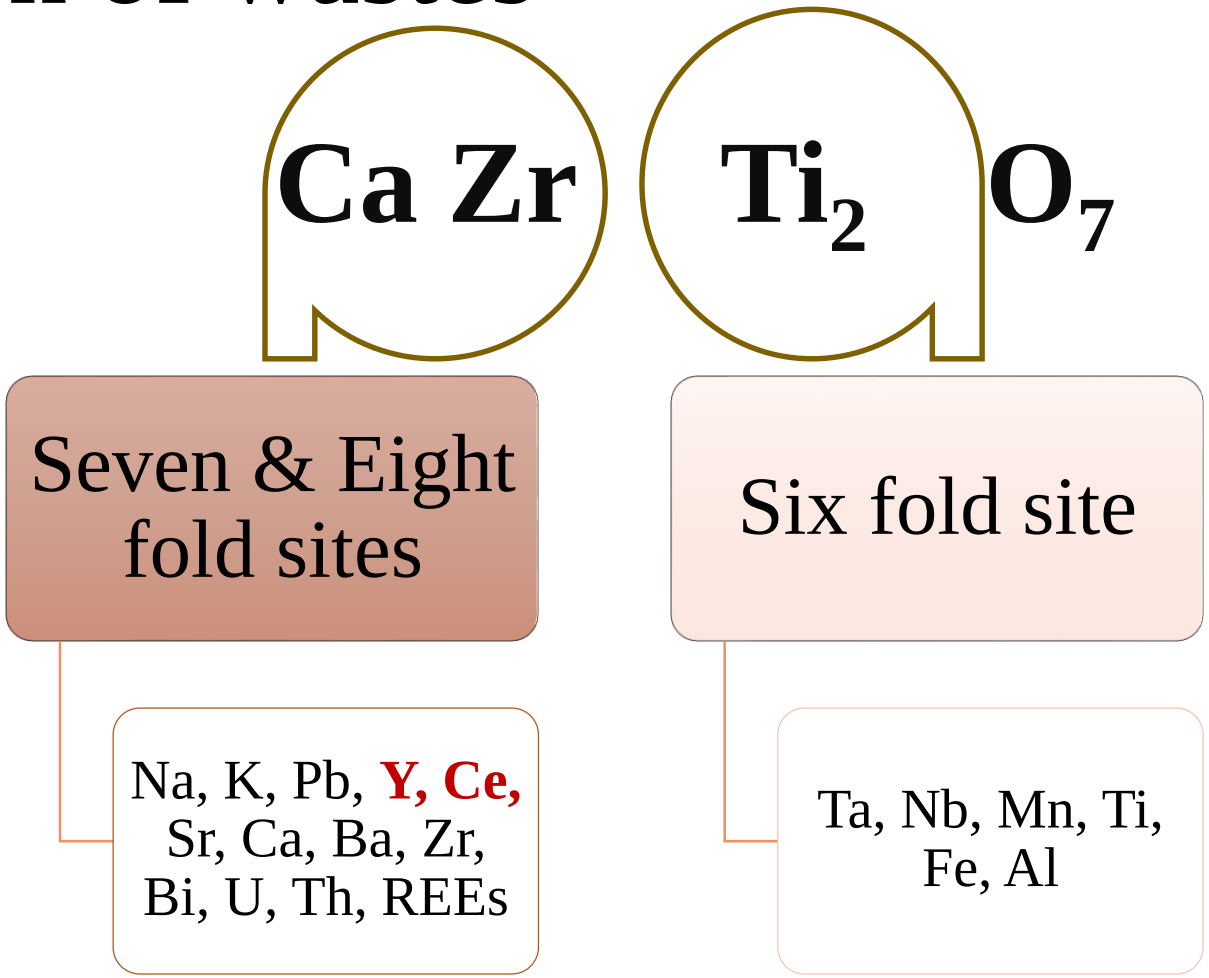
Zirconolite ($CaZrTi_2O_7$)

- Zirconolite is a promising titanate ceramic host phase for immobilization of HLWs.
- Its chemical formula is $CaZrTi_2O_7$
- Zirconolite has a monoclinic layered type structure with space group $C_{2/c.}$



Zirconolite

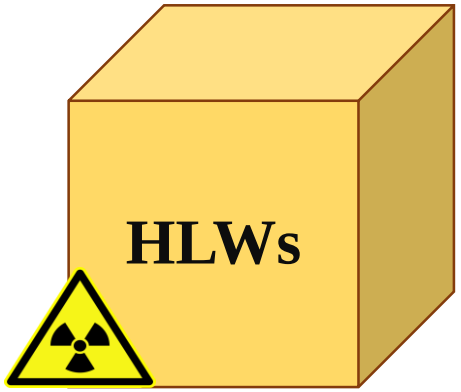
Incorporation of wastes

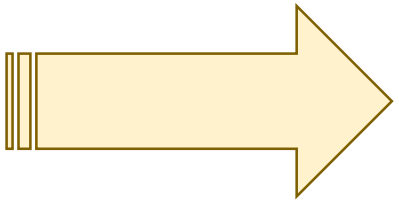


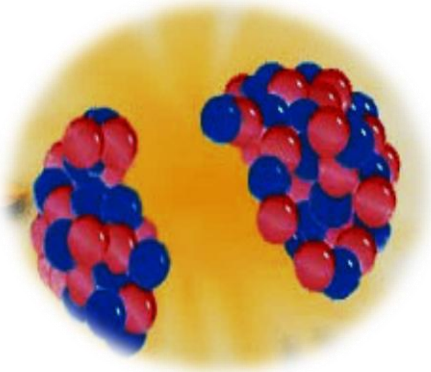
Solubility of wastes

Studied	Results	References
The phase evolution and structural relation in zirconolite composition with replacement of Ca^{2+} and Zr^{4+} by REE^{3+} (Nd, Sm, Y)	The solubility of Y^{3+} (i.e. 30 %) in 2M-Zirconolite higher compared to those of Nd^{3+} and Sm^{3+} ions (10% in both) due to fact of smaller differences in the ionic radii of cations.	M. Jafar et al. (2014) & (2016)
Synthesis and characterization of Ce-bearing zirconolite	The solubility of CeO_2 in zirconolite is about 17.5%	K. Zang et al. (2016)

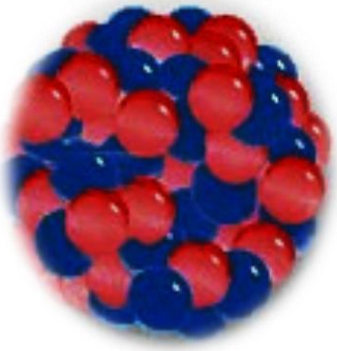
Principal sources of radiation in HLWs





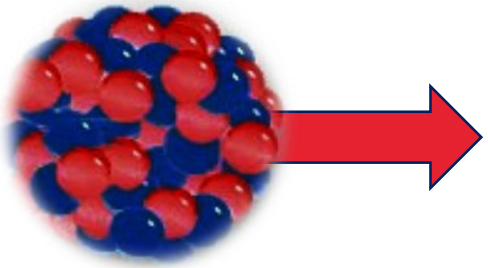


Fission fragments
70-100 MeV



Minor Actinides

α- Particle
4-6 MeV



Recoil nucleus
70-100 KeV

Radiation damage studies in material

Using neutrons from test reactor

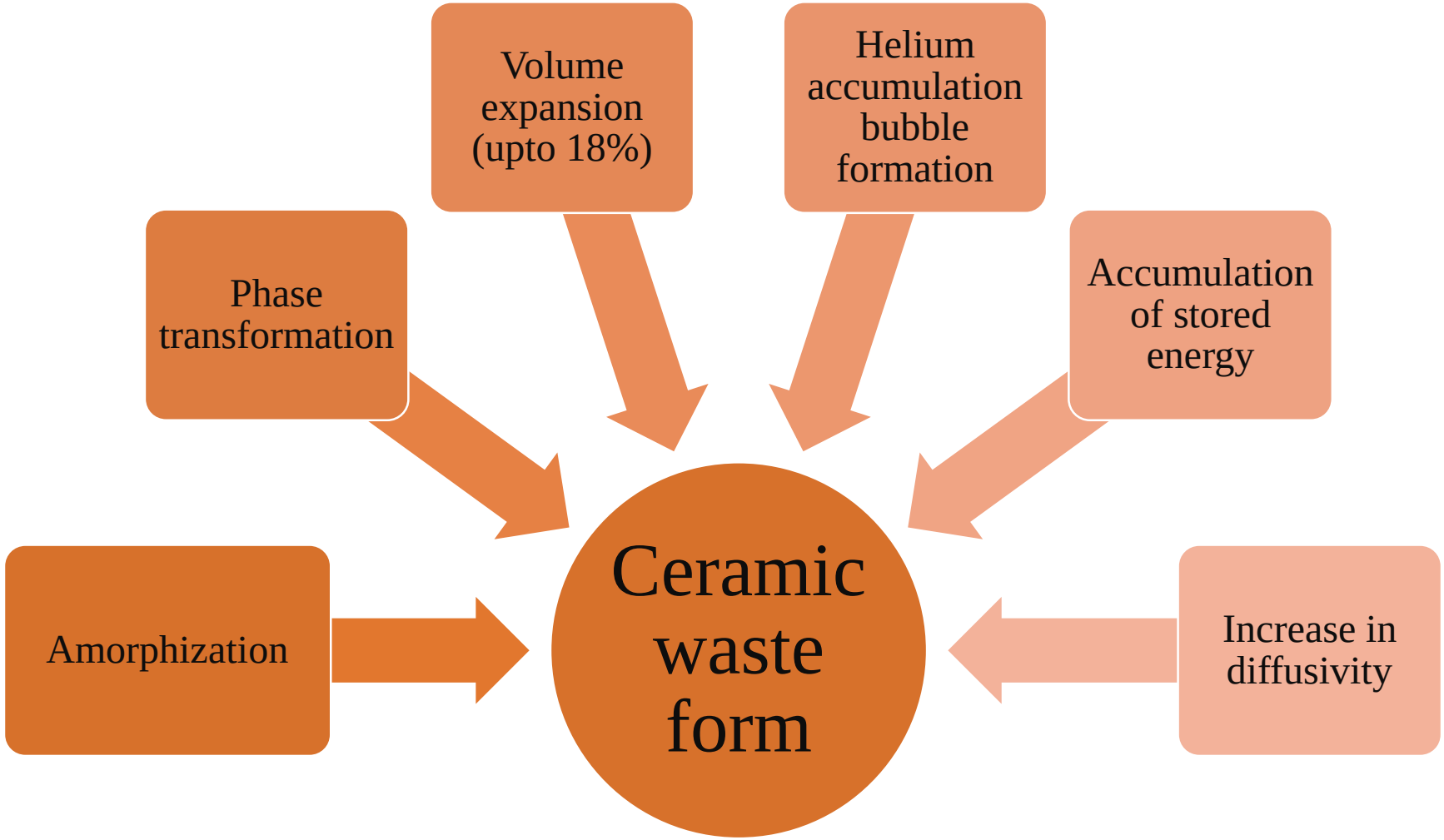
- Long test time(almost full reactor time) to achieve a desired dose.
- Highly radioactive samples
- Special facilities requires to do the characterization

Alternate

Using ion irradiation

- Short irradiation time
- Easier handing of samples
- cost effective

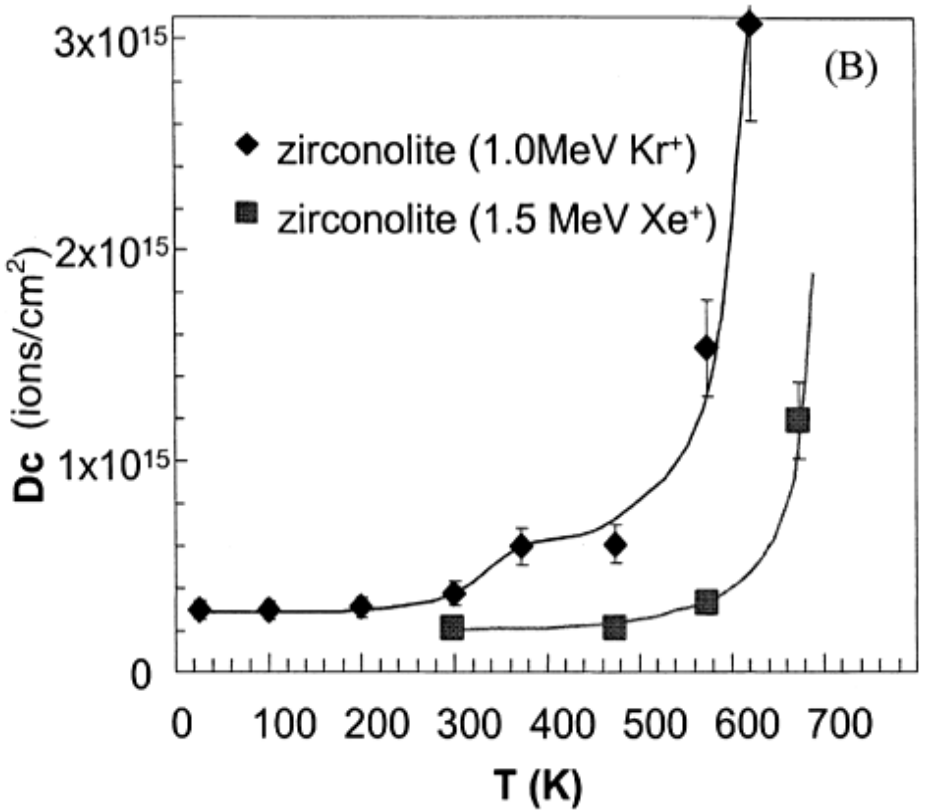
Radiation induced effects in waste forms



Simulation of α-particles

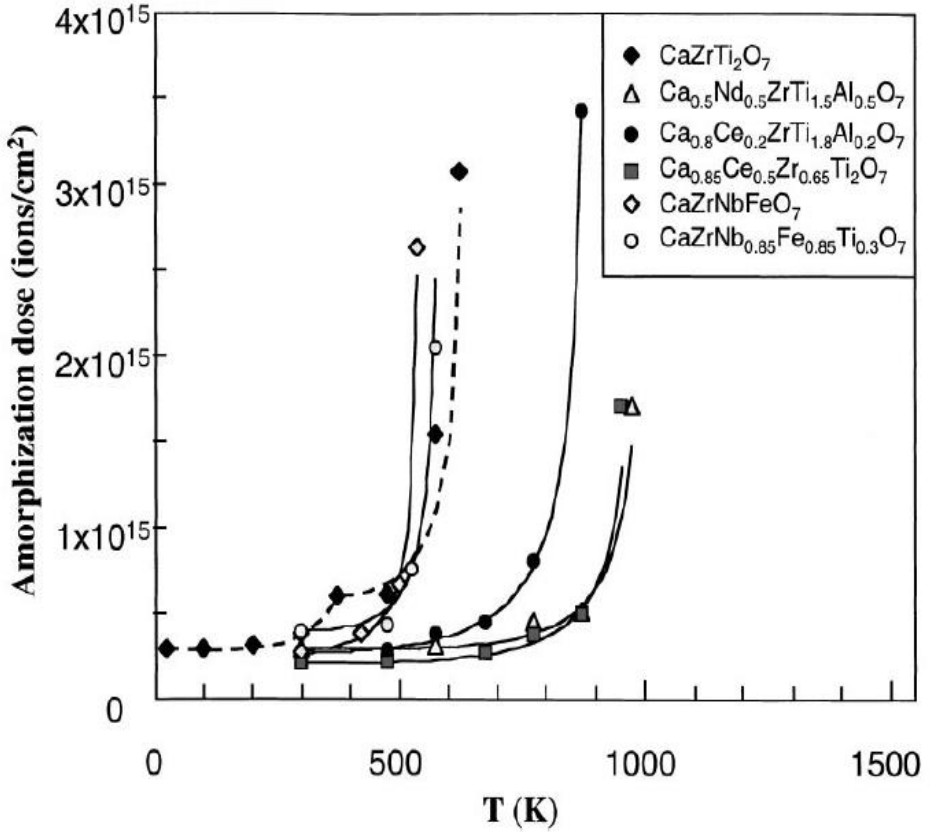
Material	Ion Beam	Temperature Range	Amorphization Dose (D_c) ions/cm^2	Other Results	References
Zirconolite	30 keV He^+ ions	Room temperature	No amorphization upto 1 x10^{17} ions/cm^2	Creation of defects/ vacancies and reduction of oxidation state	M. Gupta et.al. (2016)
Nd-doped Zirconolite	200 keV He^+ ions	Room temperature	No amorphization upto 1 x10^{17} ions/cm^2	Helium band accumulation at depth of 550-750 nm, But no amorphization	M. Gilbert et. al. (2011)

Simulation of α-recoil nucleus



***Temperature dependence of amorphization dose of zirconolite irradiated with different Ions**

* S.X. Wang *et al.* (1999)



****Temperature dependence of amorphization dose of six zirconolites**

** S.X. Wang *et al.* (2000)

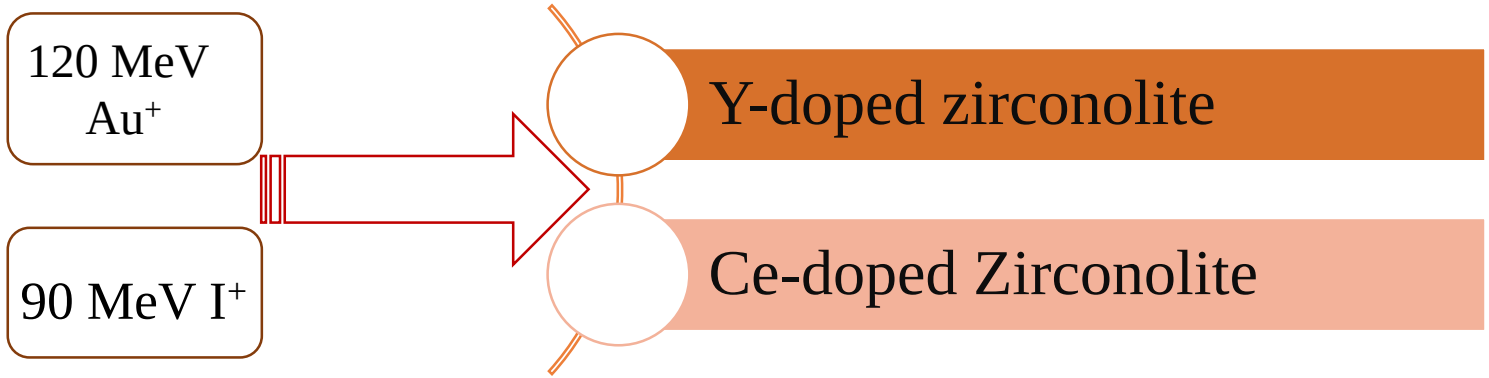
Continued…..

- The radiation induced transformation from crystalline to amorphous state in zirconolite as follows:

  Zirconolite → pyrochlore → fluorite → amorphous

- The critical temperature for amorphization depends upon the composition of zirconolite as well as mass of the ion beam.
- Amorphization dose increases with temperature.
- **In most of the studies, heavy ion beam have been used to investigate the radiation tolerance and long term stability of materials under the effects of alpha decay events.**

Research gap: SHI irradiation induced effects



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Sample	Ion	Ion energy range (MeV)	S_e (keV/nm)	S_n (keV/nm)
Ce-$CaZrTi_2O_7$	Au^+	100-200	18.93-25.22	0.3651-0.2120
	I^+	70-130	14.52- 18.11	0.1666-0.1015
Y-$CaZrTi_2O_7$	Au^+	100-200	19.39-25.72	0.3694-0.2144
	I^+	70-130	14.86-18.48	0.1687-0.1027

- Cerium is used as a surrogate for plutonium.
- Yttrium is used as a surrogate for minor actinides.

Objectives

- To study the swift heavy ion irradiation induced effects in Ce-doped zirconolite and Y-doped zirconolite at different temperatures for the production of stable and durable nuclear waste form.

- **Focused work**:

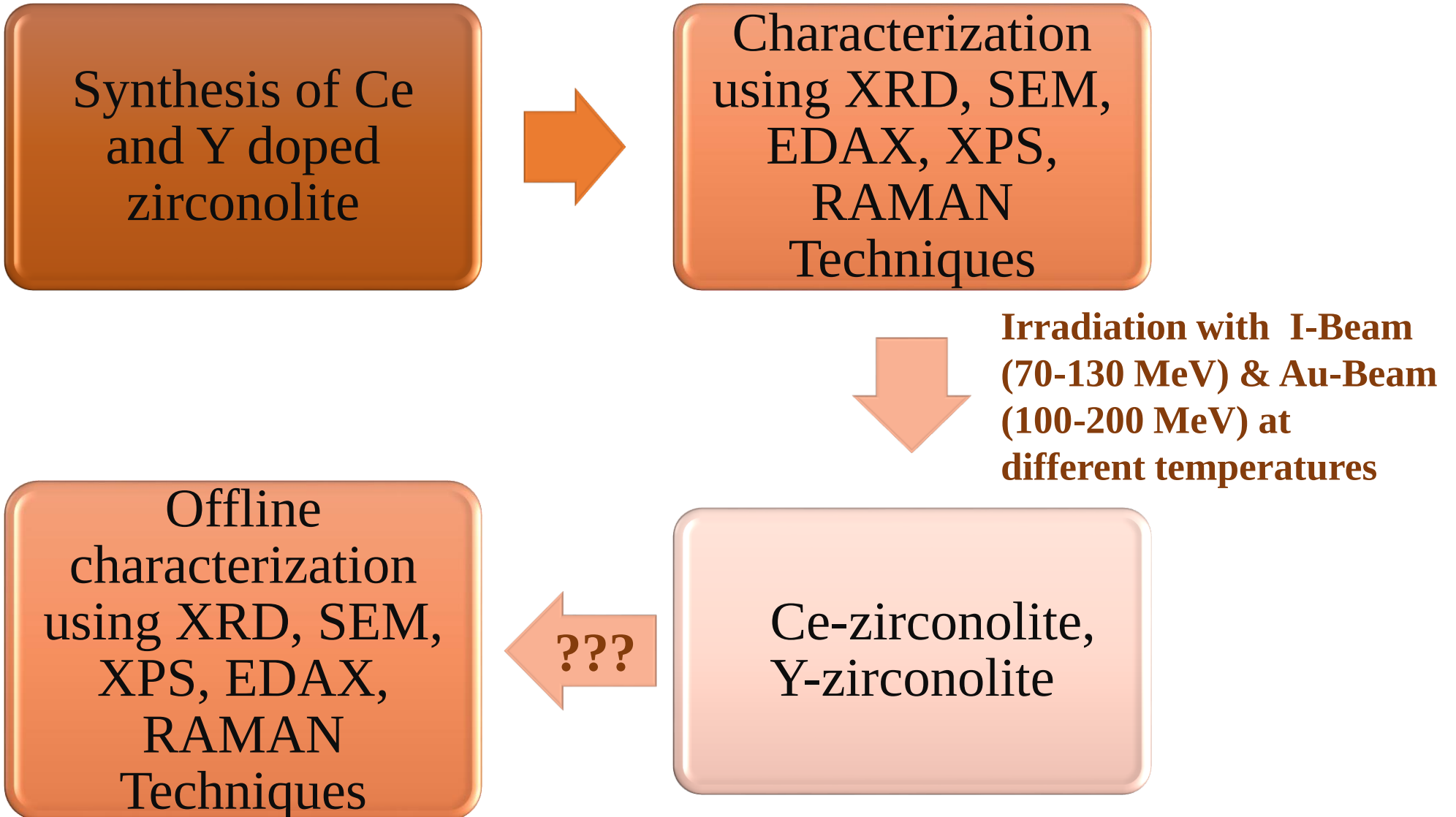
I. Structural compositions

II. Temperature

III. Ion mass & Ion energy

IV. Ion fluence

Experimental Plan



Work done so far

Synthesis:

Ce-doped Zirconolite ($Ca_{0.8}ZrCe_{0.2}Ti_{1.8}Al_{0.2}O_7$) and Y-doped zirconolite ($Ca_{0.90}Zr_{0.90}Y_{0.20}Ti_2O_7$) samples were prepared by solid state reaction method

- First sintering at 1200˚C for 16 hrs
- Second sintering at 1400˚C for 16 hrs
- With heating rate at 3 ˚C/min and Cooling rate at 2 ˚C/min

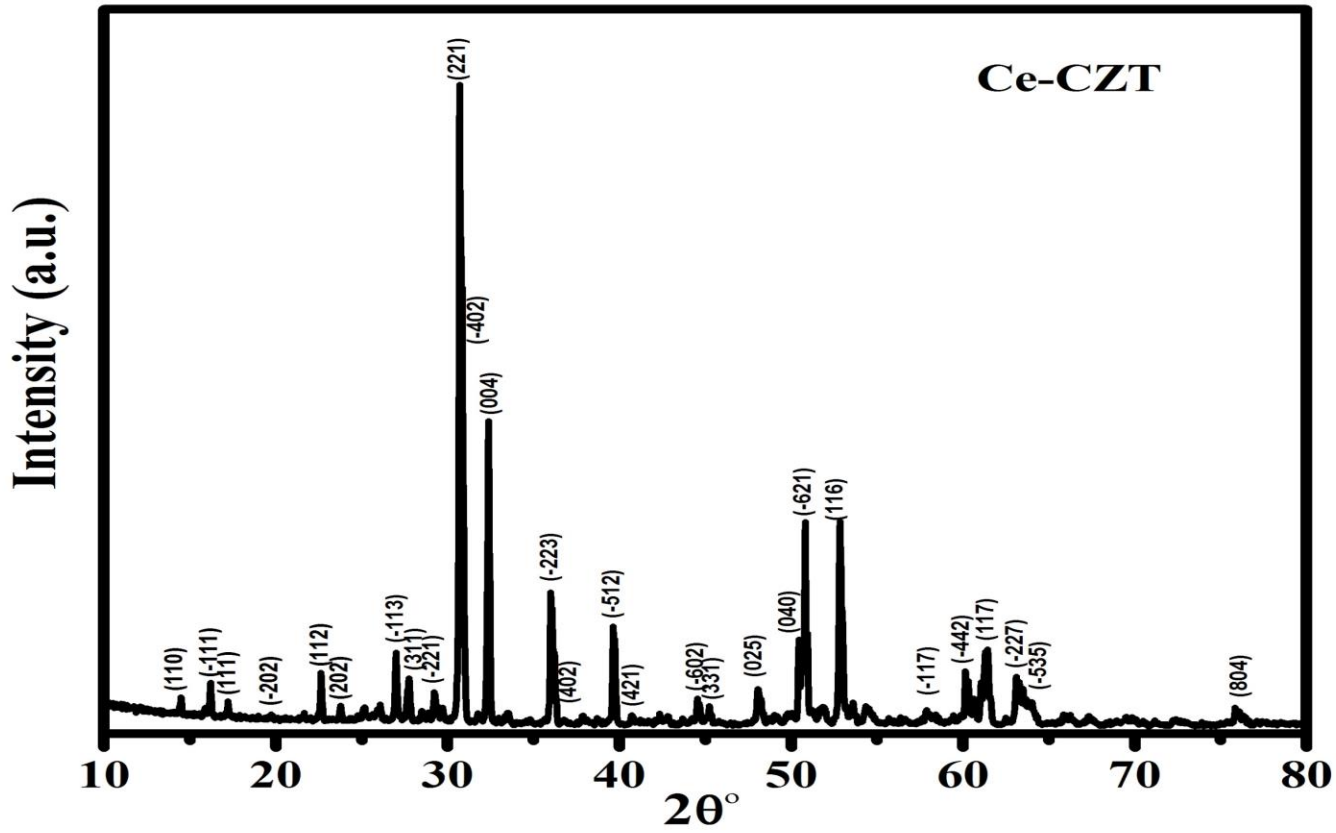
Characterization

XRD

Ce-doped Zirconolite:

- Monoclinic structure with space group $C_{2/c}$
- Lattice parameter –

a = 12.4440(2) Å, b = 7.2699(4) Å,
c = 11.4222(4) Å, β = 100.54(1)°



Thank you for your kind attention!