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Optimization of Uranium Oxide Fuel through Zirconium Alloying

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Abstract: Nuclear energy is one of the energy sources that can ensure sustainable power generation. One of the major components of a reactor that much attention needed to be given to is the fuel elements. In this work we used the computational method, the density functional theory as implemented in quantum espresso, and Boltztrap code was used to investigate the influence of Zr-UO2 on the performance of UO_2 fuel. Our understanding of UO2 fuel is that it has a low thermal conductivity by theory. Since thermal conductivity is proportional to the heat capacity, as such, it can be inferred to have a lower heat capacity. Our results shows that the thermal conductivity and heat capacity has improved as a result of the Zirconium alloying and the implementation of this is that, the new fuel will have more ability to transport heat generated by fission to the coolant and minimize burn-up. This is very necessary for nuclear safety.

Keywords: *DFT; Thermal conductivity; BoltzTraP; Reactor fuel*

1. Introduction

Nuclear energy remains a pivotal component in the global energy landscape, providing a significant share of the world's electricity with minimal greenhouse gas emissions (Prăvălie & Bandoc, (2018). The performance and safety of nuclear reactors are critically dependent on the materials used for fuel. Uranium dioxide (UO2) has long been the standard fuel material due to its high melting point and favorable neutronic properties (Costa Peluzo & Kraka, (2022). However, UO2's relatively low thermal conductivity can lead to high operating temperatures and pose challenges for reactor efficiency and safety (Skalozubov, *et al* (2020).

Recent research has focused on enhancing the thermal properties of UO2 by alloying it with various elements (Burdeinyi, *et al* (2021). One promising approach is doping UO2 with zirconium (Zr), resulting in zirconium-alloyed uranium dioxide (Zr-UO2). Zirconium doping is anticipated to improve the thermal conductivity of UO2, thereby reducing the temperature gradients within the fuel and enhancing overall reactor performance (Ortega, *et al* (2020). Additionally, the heat capacity of the fuel material is a critical factor in determining the fuel's ability to withstand and buffer temperature fluctuations during reactor operations (Liu, *et al* (2018). The Debye model was used to describe the heat capacity. This is because it provides a more accurate description of our system by considering a continuous spectrum of vibrational modes up to a maximum frequency called the Debye frequency. Mathematically, the model is described by the relation:

$$C_v = 9R\left(\frac{T}{\theta_D}\right)^3 \int_0^{\theta_D/T} \frac{x^4 e^x}{(e^x-1)^2} dx \qquad (1.1)$$

Where, R is the universal gas constant, T is the temperature and θ_D is the Derby temperature.
In the same vain, thermal conductivity in all solid materials, nuclear fuel inclusive is mainly influenced by both its electronic and phononic (lattice vibrations) contributions.
This is related by the temperature gradient as:

$$\vec{q} = -k\nabla T \qquad (1.2)$$

Where $\vec{q}$ is the heat flux vector (heat supplied per unit area), k is the thermal conductivity and ∇T is the temperature gradient. The minus sign indicate that heat flow from higher to lower temperature.
In order to predict and analyze the thermal conductivity and heat capacity of UO2 and Zr-UO2, advanced computational methods are employed. The BoltzTraP code (Madsen *et al.* (2006), implemented within the Quantum ESPRESSO suite, provides a robust framework for such investigations. BoltzTraP leverages on the output of density functional theory, taking the band structure dependent parameters and using it to determine the transport properties.
This study aims to provide a comparison of the thermal conductivity and heat capacity of UO2 and Zr-UO2 using the BoltzTraP code. By integrating density functional theory (DFT) calculations within Quantum ESPRESSO (Woods, *et al,* (2019), we seek to explore the impact of zirconium doping on the thermal properties of uranium dioxide. The insights gained from this research will inform the development of advanced nuclear fuels with enhanced performance and safety profiles, contributing to the optimization of nuclear reactor operations and the sustainability of nuclear energy.

Computational Details

In this article we have employed the density functional theory method to study the transport properties of UO2 and Zr-UO2. For this work, the BoltzTraP code integrated with the quantum espresso (Giannozzi, *et al*. (2020). was used to solve the semiclassical Boltzmann equation to obtain the thermal conductivity and heat capacity. Firstly, a self-consistent field DFT was performed on the pristine material to obtain the ground state electron density with a kpoints mesh of 4x4x4 and thereafter we perform a non-self-consistent field calculation with a dense k-mesh of 12x12x12 to obtain the band structure dependent parameters. For the Zr-UO2, the alloyed material was relaxed and then and calculations were performed as in the pristine material 7x7x9 and 14x14x18 kmesh for scf and nscf calculation respectively. It is noteworthy to say that we performed a DFT+U calculations in both cases with 4.0eV as the hubbard correction used to delocalized the 5f and 4d orbitals of uranium and Ziconium respectively. The generalized gradient approximation (GGA) functional was used and the Perdew Burke Erzhenhorf (PBE) was employed to handle the exchange correlation (Arshad Javid, *et al.* (2018).

Results and Discussions

Many investigations have proven that UO2 has a low thermal conductivity; this effect will actually pose a negative effect on its performance as a fuel material. UO2 is the most commonly used nuclear fuel in commercial nuclear reactors. Its behavior under reactor conditions is well understood, and extensive operational data are available (Gamble, *et al.* (2021), (Ortega, *et al*. (2022), and (Rest, (2019) The fuel has proven technology, with a high melting point (~2800°C), chemical stability, moderate thermal conductivity, and radiation resistance.

Several factors are crucial for efficient nuclear fuel, with higher thermal conductivity being a primary focus. Higher thermal conductivity is critical because it facilitates efficient heat transfer from the fuel to the coolant, thereby maintaining the structural integrity of the fuel. Overheating can lead to fuel damage, posing risks to the reactor. Higher thermal conductivity fuels enhance reactor safety (Zhou, & Zhou, (2018).

Thermal conductivity significantly influences temperature distribution and thermal management within the reactor. These thermal effects affect neutron flux by influencing factors such as Doppler broadening, material integrity, reactor stability, and fuel burn up patterns (Liu, *et al.* (2019).

To enhance fuel efficiency, an alloy fuel using Zr with UO2 is developed. Zr is chemically compatible with UO2 and has significantly higher thermal conductivity compared to UO2. The alloy is formed by substituting

50% of U with Zr, resulting in $UZrO_4$. The heat capacity and thermal conductivity of this new alloy fuel are measured and compared with UO_2, as shown in Figures 1 and 2

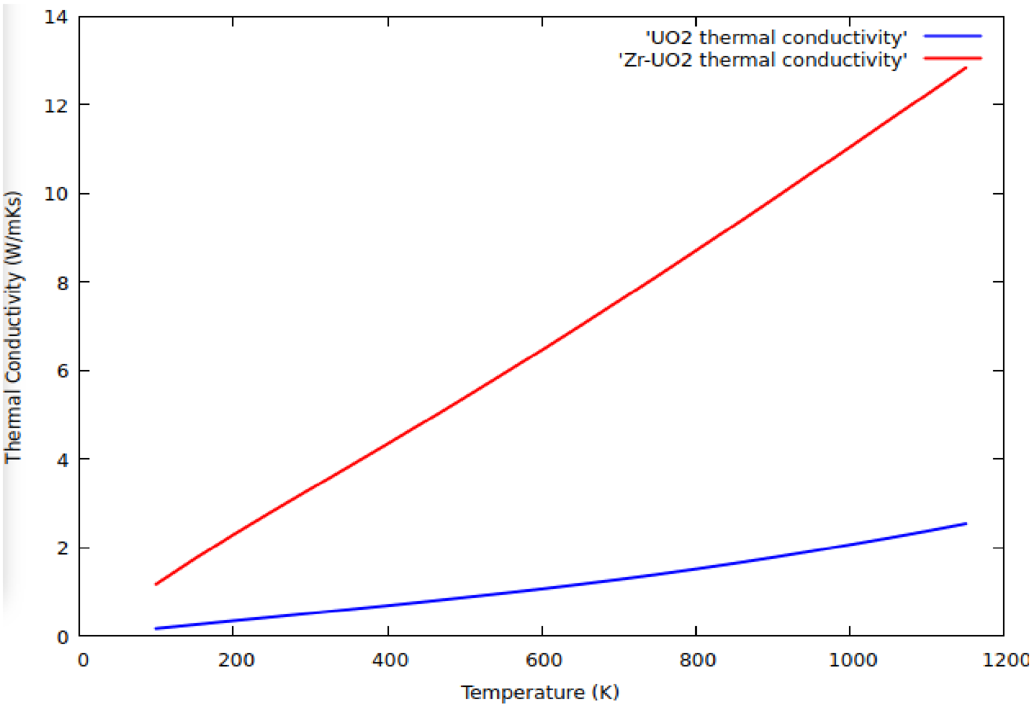

Figure 1 : Thermal Conductivity of UO2 and Zr-UO2

The heat capacity and thermal conductivity of the new fuel $UZrO_4$ are superior to those of UO_2. This demonstrates that the new fuel alloy has the potential to improve the efficiency of nuclear fuel, thereby boosting overall reactor performance, enhancing safety, and improving economy.

Thermal Conductivity

From our result in figure 1 and 2, we have discovered the Zr-UO2 will perform better than the UO2 fuel. The necessity of a better fuel has many consequences in reactor safety operation.

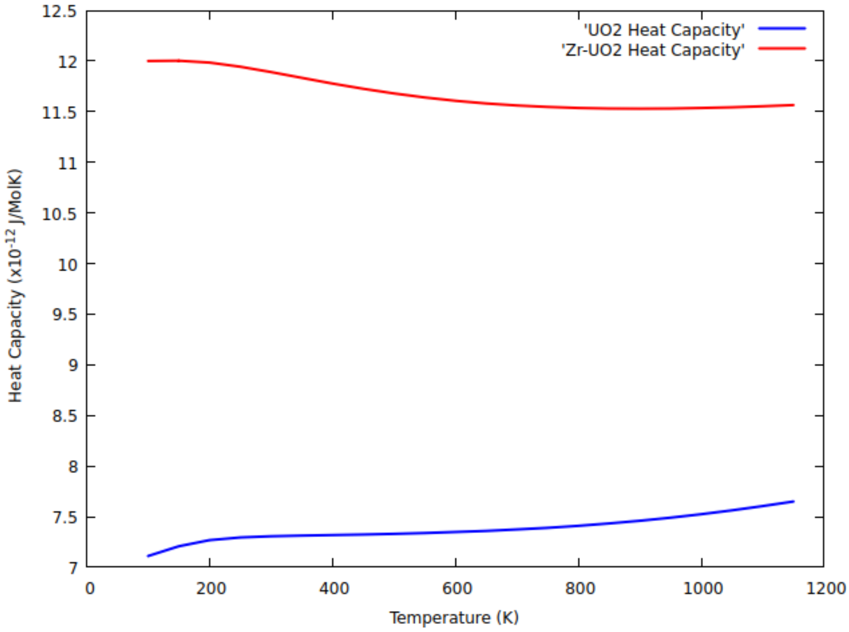

Figure 2 : Heat Capacity of UO2 and Zr-UO2

Looking at figure 1 where the thermal conductivity of the UO2 is very low, this was established in the literatures according to Ševeček, *et al.* (2018), implies that it cannot efficiently transport heat across its length to the coolant. Now in nuclear reactor, heat is generated in the core, but not meant to remain in the core. Reactor functions efficiently when heat generated are removed accordingly and the medium to which the heat can be removed is the fuel element. If the thermal conductivity of a fuel material is low, the fuel cannot efficiently transport heat from the core to the coolant, as such heat within the core will be greater than heat removed, and this scenario can lead to fuel meltdown. In our result we carefully studied the effect Zirconium on the performance of UO2 fuel, doping increase its performance as seen in figure 1, this means that alloying Zr with U improved the thermal transport property. This will no doubt enhance the strength of the new fuel.

The Zr-UO2 fuel have an improved thermal conductivity according to our results and this also agrees with Frost, et al. (2020). With this enhancement we can be confident that fuel meltdown will be less pronounced in the new fuel as compared to the original fuel and more so, in the aspect of reactor safety, heat removal will be high in this new fuel of ours because of its improved thermal conductivity. This thermal conductivity, as earlier established is the ability of the fuel to transport heat to the coolant, there by maintaining the optimum fuel temperature. At a fuel temperature of 800°C close to the fuel centerline, the values of thermal conductivity of the UO2 and Zr-UO2 was found to be 1.8 and 8.2 W/mK respectively.

Heat Capacity

Another factor that affects the performance of a fuel is its heat capacity. Heat capacity is the heat required to raise the temperature of a fuel material. When a fuel retains heat without burning up, the fuel is good. In our own case, we are looking at this from, the point of the fuel burn up, when a fuel absorb heat above the fuel temperature, it is likely that the fuel will begin to burn due to excess heat. For instance, in a transient condition, where the temperature changes with time, the change in temperature when particularly it's above the fuel temperature will cause the fuel to begin to burn up. This is one of the issues that this work wants to address, we saw from our result how the Zr-UO2 performs better in terms of ability to retain heat. This for us is a breakthrough because, if we imagine at say 800°C the heat capacity of UO2 and Zr-UO2 are 7.8 $x10^{-12}$ and 11.5 $x10^{-12}$ J/molK respectively, it means that Zr-UO2 will hold heat with minimal burn- up. We report minimal because other fuels may have improved properties than this. In figure 2 above, the difference between the performance of UO2 and Zr-UO_2 at 800°C or 1073k is about 68%, this shows that Zr-UO2 can perform 68 times as fuel material compared with UO_2.

Conclusion.

We have studied computationally using the density functional theory (DFT) as implemented on the quantum Expresso code, the effect of the Zr on the performance of UO2 fuel. The Boltztrap code was able to predict how the behavior of UO2 fuel changes when alloyed with Zr. The consequence of this is that Zr-UO2 improves the fuel thermal conductivity, giving it an advantage over UO2 in removing heat from the core to the coolant thereby ensuring a safe reactor operating environment. Also, our results show that the heat capacity of the Zr-UO2 has the tendency to minimize fuel burn-up. In conclusion, we envisage that fuel material properties can be enhanced through alloying. This is one way of optimizing fuel materials to promote safety in reactor operations.

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Compliance with Ethical Standards: This article does not contain any studies involving human or animal subjects.

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