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Fabrication of lanthanum-doped thorium dioxide by high-energy ball milling and spark plasma sintering

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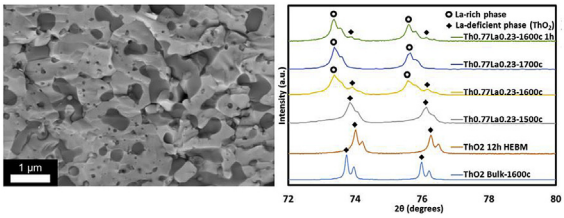
HIGHLIGHTS

- Lanthanum incorporation into ThO_2 by high energy ball milling and rapid consolidation by spark plasma sintering.
- Elucidation of phase behavior of the La-doped ThO_2 and the contributions of La incorporation and SPS sintering conditions.
- Investigation of the effects of La incorporation and high energy ball milling on the thermal behavior of La-doped ThO_2.

GRAPHICAL ABSTRACT



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ABSTRACT

Abstract: High-energy ball milling was used to synthesize $Th_{1-x}La_xO_{2-0.5x}$ ($x = 0.09, 0.23$) solid solutions, as well as improve the sinterability of ThO_2 powders. Dense La-doped ThO_2 pellets with theoretical density above 94% were consolidated by spark plasma sintering at temperatures above 1400 °C for 20 min, and the densification behavior and the non-equilibrium effects on phase and structure were investigated. A lattice contraction of the SPS-densified pellets occurred with increasing ball milling duration, and a secondary phase with increased La-content was observed in La-doped pellets. A dependence on the La-content and sintering duration for the onset of localized phase segregation has been proposed. The effects of high-energy ball milling, La-content, and phase formation on the thermal diffusivity were also studied for La-doped ThO_2 pellets by laser flash measurement. Increasing La-content and high energy ball milling time decreases thermal diffusivity; while the sintering peak temperature and holding time beyond 1600 °C dramatically altered the temperature dependence of the thermal diffusivity beyond 600 °C.

1. Introduction

Thorium has drawn the attention of the nuclear community due to the potential implications of thorium fuel cycle, particularly on potentially-improved operational safety and non-proliferation. The thorium fuel cycle is based upon the fertile nature of Th^{232}, the sole isotope existing in a significant quantity in nature, and its transmutation to fissile U^{233}. The major benefits of the thorium fuel cycle are derived from the material properties of thorium, including the high melting point of ThO_2 (3390 °C) as compared to that of uranium dioxide (2865 °C), as well as increased thermal conductivity in ThO_2

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over UO_2 and its lower thermal expansion [1,2]. The oxidation behavior of thorium as a 4 + oxidation state as compared to uranium's 4+, 5+, and 6 + oxidation states benefits the fabrication and chemical stability of the fuel. The attractiveness of the thorium fuel cycle is further enhanced by the relative abundance of thorium as compared to uranium, with thorium being three to four times as common globally [1,2]. The thorium fuel cycle has drawn attention for being proliferation resistant due to difficulties in the acid dissolution of ThO_2 as a result of the aforementioned chemical stability, and the high content of gamma-emitting U^{232} present in spent ThO_2 fuels [1–4]. However, drawbacks associated with the thorium fuel cycle, such as the necessity of reprocessing to fully utilize the benefits of the fuel cycle, and difficulties with such reprocessing due to the aforementioned chemical stability and high gamma-emissions, have resulted in a delayed implementation of thorium technologies.

While the majority of work pertaining to ThO_2 mixtures has focused on the combination of ThO_2 and major actinides in mixed oxide (MOX) fuels [5–8], the incorporation of lanthanides into the ThO_2 matrix has been an ongoing research topic for the nuclear community. Incorporation of lanthanides into ThO_2 has been previously researched with the goal of improving the performance of the ThO_2-lantainide systems for applications primarily related to nuclear fuels. Prior investigations have focused on the effects of lanthanide dopants on the chemical stability [9], thermal conductivity [10,11], thermal expansion [12], lattice parameter [13], and densification [14] of ThO_2-lanthanide systems.

In this study, the incorporation of the lanthanide into the ThO_2 systems was achieved by a low temperature solid-state reaction by high energy ball milling (HEBM). HEBM is a room temperature solid-state synthesis technique which allows for the simultaneous reduction of particle size and facilitation of phase transformations and/or incorporation of additives. HEBM has been previously utilized for the synthesis of nuclear fuels [15], photocatalysts [16], fuel cells [17], and nuclear waste forms [18]. HEBM was used in this study as the primary means of incorporating dopants into the ThO_2 matrix, and the additional effect of mechanically reducing the particle size allowed for a simple variation in starting particle sizes.

The dense La-doped ThO_2 pellets were consolidated by spark plasma sintering (SPS). SPS is a field-assisted sintering technique (FAST) which enables the reduction in the temperature and hold times required for densification; this creates the potential to fabricate fully-densified ceramics with significant reductions of energy cost as compared to conventional techniques [19,20]. SPS, as a rapid consolidation technology, has attracted extensive attention in nuclear communities for fabricating advanced nuclear fuels. For example, SPS has been utilized in sintering high-density ThO_2 [21], UO_2 [22], and CeO_2 [23].

This work outlines the procedure to synthesize nano-sized ThO_2 powders, both with and without incorporating lanthanum oxide, through HEBM as well as the sintering routine to produce fully densified ThO_2 and $Th_{1-x}La_xO_{2-0.5x}$ pellets via SPS. SPS was used to not only densify the ThO_2 and $Th_{1-x}La_xO_{2-0.5x}$ powders, but investigate the effect of non-equilibrium conditions during sintering of doped samples. The effects of the dopant content, milling time, and sintering parameters on ThO_2 sinterability and pellet densification were investigated. The structure and phase evolution including the phase formation and the secondary phase segregation due to non-equilibrium conditions during synthesis and sintering, and their effects on thermal-physics properties were also investigated.

2. Experimental details

2.1. La incorporation and ThO_2 powder fabrication

Nano-sized powders of La-doped ThO_2 were fabricated via HEBM (Fritsch, Pulverisette 7 Premium Line, Idar-Oberstein, Germany). Thorium dioxide (99.9% purity; International Bio-Analytical Industries Inc.) and lanthanum oxide (99.99% purity; Acros Organics) powders were used without further purification. Powders were mixed at weight ratios corresponding to the desired atomic ratios, and 10 g of mixture was loaded into the milling jars in 10 ml of ethanol. HEBM was carried out using a zirconia bowl (80 ml) and balls (1.5 mm diameter) for 12 h–18 h milling time at 600 rpm, with a milling pattern of 15 min on, 5 min off, to prevent overheating of the ball mill, until the mixture was determined to be homogeneously blended by x-ray powder diffraction.

2.2. Spark plasma sintering

Spark plasma sintering was carried out using a Dr. Sinter® SPS-211 Lx system with a procedure similar to our previous work [15]. To prepare each sample, approximately 1 g of powder was loaded into a graphite die, 10 mm in diameter. Graphite paper (0.20 mm thick) was used to envelope the powders, ensuring proper fit during assembly, ease of sample retrieval after sintering, and sufficient contact to facilitate the current passing through the assembly. The die was then wrapped in a graphite felt to insulate the die from radiative heat loss during fabrication. The fully assembled graphite die was then arranged between graphite spacers, and loaded into the SPS between the rams of the hydraulic press with an applied pressure of 10 MPa.

Sintering was conducted under flowing argon, with current applied in a 25 ms on, 3 ms off pulse pattern. The sample temperature, which was measured using a pyrometer, was gradually increased from 25 °C to 600 °C before being increased to the peak temperature (between 1300 °C and 1700 °C) at a rate of 100 °C/min (Fig. 1). The uniaxial pressure applied by the hydraulic press was increased to 40 MPa at a rate which allowed it to reach its maximum value simultaneously with the temperature. The peak temperature was held at for a set period of time, (5 min unless otherwise noted) and then cooled to 100 °C below the peak temperature at a rate of 20 °C/min. The applied pressure was reduced during this cooling to 10 MPa at a rate of 6 MPa/min. The sample was then held at this reduced temperature for another 5 min, before being allowed to cool freely under the flowing argon.

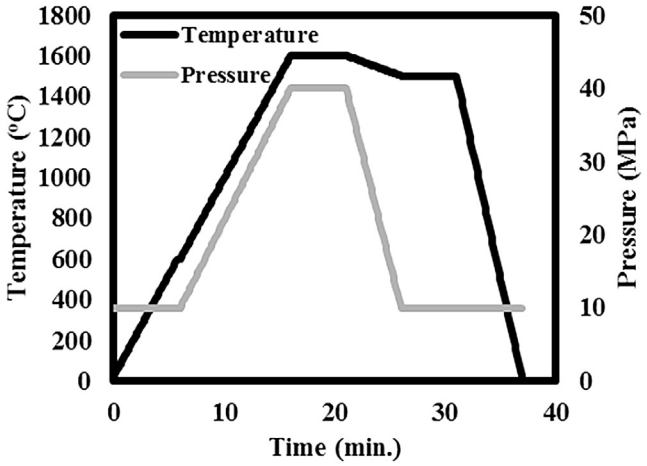

Fig. 1. Typical spark plasma sintering temperature-pressure profile used to density ThO_2 powders. The maximum temperature was reached at a heating rate of 100 °C/min and maintained for 5 min.