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Optical properties of dense zirconium and tantalum diborides for solar thermal absorbers

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ABSTRACT

Ultra-high temperature ceramics (UHTCs) are interesting materials for a large variety of applications under extreme conditions. This paper reports on the production and extensive characterization of highly dense, pure zirconium and tantalum diborides, with particular interest to their potential utilization in the thermal solar energy field. Monolithic bulk samples are produced by Spark Plasma Sintering starting from elemental reactants or using metal diboride powders previously synthesized by Self-propagating High-temperature Synthesis (SHS). Microstructural and optical properties of products obtained by the two processing methods have been comparatively evaluated. We found that pure diborides show a good spectral selectivity, which is an appealing characteristic for solar absorber applications. No, or very small, differences in the optical properties have been evidenced when the two investigated processes adopted for the fabrication of dense TaB_2 and ZrB_2, respectively, are compared.

1. Introduction

The so-called "energy problem" is one of the major challenges to address in the next future. Solutions will compulsorily include renewable energies, and in particular solar energy exploitation, because energy must be supplied to a growing world population in a safe, environmental-friendly and sustainable way. In this regard, solar thermal technology [1] shows efficiencies intrinsically higher than photovoltaic one. The scheme of concentrating the solar power to a central tower [2] is considered one of the most promising, as it additionally can exploit mature technologies of conventional fossil fuels plants. However, it is important to increase the operating temperature of the plants to improve the efficiency of their thermal cycles. In this context, the solar radiation receiver is a critical element. In particular, several requirements have to be satisfied [3–5], like a high solar absorbance, to efficiently absorb sunlight, a low thermal emittance, to limit thermal re-radiation losses, and good thermal properties, to properly transfer the thermal energy to the exchange medium. Thus, the main challenge for increasing the operating temperature of thermal plants is the development of novel receiver materials which are stable at very high temperatures and able to exhibit all the favorable optical and thermal properties mentioned above.

To this aim, particular attention has been recently focused on the group of materials known as Ultra-High-Temperature-Ceramics (UHTCs), which includes carbides, borides and nitrides of early transition metals and are characterized by very high melting temperatures (above 3200 K). UHTCs are known to be ideal materials for thermal protection systems, especially those requiring chemical and structural stability at extremely high operating temperatures thanks to their solid state stability, good thermochemical and thermomechanical properties, high hardness, high electrical and thermal conductivities [6–8]. In this regard, some relevant structural, thermodynamic, physical, and mechanical properties of two of the most representative UHTCs, namely ZrB_2 and TaB_2, are summarized in Table 1. Historically, UHTCs are mainly employed in the aerospace industry for hypersonic vehicles, rocket motor nozzles or atmospheric entry probes capable of the most extreme entry conditions [6–8]. In addition to this application, in the last few years they have been also proposed as possible candidates for novel

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Table 1
Properties of ZrB_2 and TaB_2.

Property	ZrB_2	TaB_2
Crystal system space group prototype structure a (Å) c (Å)	Hexagonal P6/mmm AlB_2 3.17 3.53 [6]	Hexagonal P6/mmm AlB_2 3.0880 3.2410 [25]
Density (g/cm^3)	6.119 [6]	12.568 [25]
Enthalpy of formation, at 25 °C (kJ/mol)	−322.6 [6]	−209.200 [26]
Free energy of Formation, at 25 °C (kJ)	−318.2 [26]	−206.7 [26]
Melting temperature (°C)	3245 [6]	3037 [27]
Coefficient of Thermal Expansion (K^{-1})	5.9×10^{-6} [6]	8.2×10^{-6} [28]
Heat capacity, at 25 °C (J (mol K)$^{-1}$)	48.2 [6]	33.92 [29]
Electrical conductivity, at 25 °C (S/m)	1.0×10^7 [6]	3.03×10^6 [30]
Thermal conductivity (W·(m k)$^{-1}$)	60 [6]	16.0 [28]
Young's Modulus (GPa)	489 [6]	248.2 [29]
Hardness (GPa)	23 [6]	19.6 [31]

solar absorbers able to operate at very high temperature, because of their favorable optical and radiative properties like intrinsic spectral selectivity and low thermal emittance [9–11]. In fact, it is well established that spectral selectivity is a key parameter for increasing the efficiency of solar thermal systems [12]. In addition to that, it should be also mentioned the importance of a high solar absorbance, which represents, on the other hand, a possible criticism for UHTCs, as this property is generally lower, for instance, than that of silicon carbide (SiC). However, it has been recently demonstrated, for the case of hafnium carbide [11], that surface texturing can selectively increase solar absorbance without detrimentally affecting thermal emittance.

As for borides, optical and structural properties of several materials belonging to this family, including additive containing ZrB_2 and TaB_2, have been recently investigated and appealing characteristics for solar absorber applications have been found [13–16]. Despite of their attractive properties, the refractory character of Zr and Ta borides makes powder consolidation very difficult, particularly when taking advantage of conventional pressure assisted sintering methods, where holding temperatures even above 2300 K and prolonged times (hours) are typically needed [6,17]. Nevertheless, materials with residual porosity and coarse microstructure are often obtained under such processing conditions. Therefore, various approaches have been proposed to overcome this problem. In this regard, the use of innovative densification techniques, like the Spark Plasma Sintering (SPS) or other electric current assisted consolidation methods, was demonstrated particularly advisable for processing difficult-to-sinter materials [18]. The same technology was also successfully adopted for reactive sintering purpose, through the so-called Reactive SPS (RSPS) [19–22]. Furthermore, the SPS conditions can be further mitigated if starting from powders with high sintering ability. To this aim, it was found that the use of powders prepared by Self-propagating High-temperature Synthesis (SHS) leads to higher density samples, with respect to materials with the same nominal composition obtained using alternative preparation routes [23,24].

In this work, the optical properties of dense and monophasic ZrB_2 and TaB_2 are investigated for the first time, to the best of our knowledge. Both borides have been produced using the two different RSPS and SHS/SPS techniques. Microstructural and optical characteristics of the resulting products have been compared.

2. Experimental procedure

A Spark Plasma Sintering (SPS) equipment (515 model, Sumitomo Coal Mining Co Ltd, Japan) was used under mild vacuum conditions (20 Pa) to obtain TaB_2 and ZrB_2 dense samples by reactive (RSPS) or non-reactive sintering. In the latter case, transition metal diborides were preliminarily synthesized by SHS and the obtained powders consolidated by SPS. Such two steps processing route will be hereafter indicated as SHS/SPS. Initial mixtures consist of B (Sigma–Aldrich, amorphous, particle size < 1 μm, ≥ 95% purity), Zr (Alfa Aesar, particle size < 44 μm, 98.5% purity) or Ta (Alfa-Aesar, particle size < 44 μm, 99.6% purity) combined according to the reaction $Me + (2 + x) B \rightarrow MeB_2$, where Me = Zr or Ta. The use of a slight excess of B ($x = 0.1$) with respect to the stoichiometric value was aimed to remove some oxide impurities originally present in the raw materials, particularly in Zr powders. SHS reactions, performed under Ar atmosphere, were locally activated using an electrically heated tungsten coil. Further details on the SHS procedure can be found elsewhere [32]. The obtained porous samples were ball milled for 20 min to provide powders with average particle sizes of approximately 6.7 and 1.5 μm for ZrB_2 and TaB_2, respectively.

Dense samples with 14.7 mm diameter and about 3 mm thickness were produced by SPS starting from proper amounts of ZrB_2 and TaB_2 powders (SHS/SPS) or elemental reactants (RSPS). During the consolidation process, the applied current was increased from zero to $\bar{I} = 1300$ A in 10 min. Then, the $\bar{I}$ value was maintained constant for additional 20 min. The applied mechanical pressure was generally set in the range 50–60 MPa, except for the case of the ZrB_2 system processed by RSPS, where relatively lower loads (20 MPa) were used. This was to avoid some drawbacks (rapid gas development, product inhomogeneity, etc.) and safety problems (die/plunger breakage, etc.) encountered when the strongly exothermic reaction for the ZrB_2 formation from its elements was