# Vacancies and substitutional defects in multicomponent diboride $Ti_{0.25}Zr_{0.25}Hf_{0.25}Ta_{0.25}B_2$

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## 1 Introduction

Diborides of early transition metals are famous for their ultra-high hardness, high melting temperature, and electrical conductivity. Single-phase high-entropy (multicomponent) diborides have attracted attention recently due to a further enhancement of hardness, thermal stability, or oxidation resistance, allowing them to be used in high-temperature environments with special requirements such as a combination of electrical conductivity with high hardness.

Together with their preparation as bulk materials, these diborides are studied in the form of thin films, prepared usually by magnetron sputtering (Farhadizadeh *et al.* 2022). This thermodynamically non-equilibrium technique leads to presence of a variety of defects of the hexagonal crystal structure of the grown films, *e.g.* vacancies, substitutional or interstitial defects, or stacking faults. The present contribution aims to characterise boron vacancies and carbon substitutions in detail and to shed light on their effect on the material properties, using $Ti_{0.25}Zr_{0.25}Hf_{0.25}Ta_{0.25}B_2$ (Feng *et al.* 2021) as a test case (Matas *et al.* 2022).

## 2 Method

Density-functional theory was used to compare formation energies of $Ti_4Zr_4Hf_4Ta_4B_{32}$ (Fig. 1a), $Ti_4Zr_4Hf_4Ta_4B_{32-x}$, and $Ti_4Zr_4Hf_4Ta_4B_{32-x}C_x$ where $0 \leq x \leq 16$. For each $x$, a wide range of possible defect distributions was investigated (*e.g.*, see Fig. 1b for $Ti_4Zr_4Hf_4Ta_4B_{26}$ with B vacancies as close to each other as possible). For selected compositions and defect distributions, electronic densities of states and mechanical properties were calculated.

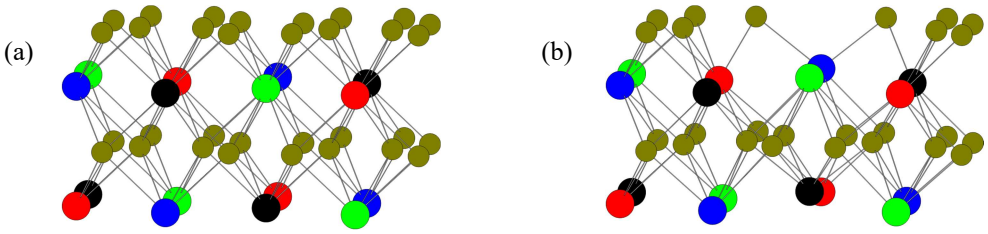


**Figure 1:** Periodic simulation cells of $Ti_4Zr_4Hf_4Ta_4B_{32}$ (perfect crystal; a) and $Ti_4Zr_4Hf_4Ta_4B_{26}$ with coalesced vacancies (planar void; b). Dark yellow balls represent B atoms.

## 3 Results

Although both boron vacancies and carbon substitutions at boron sites are readily produced by non-equilibrium thin-film deposition techniques (despite being thermodynamically unfavourable according to the material formation energies), the former type of point defects was found to be more preferred than the latter. In addition, boron vacancies tend to coalesce into a larger planar void, minimising the number of broken B–B bonds, while carbon

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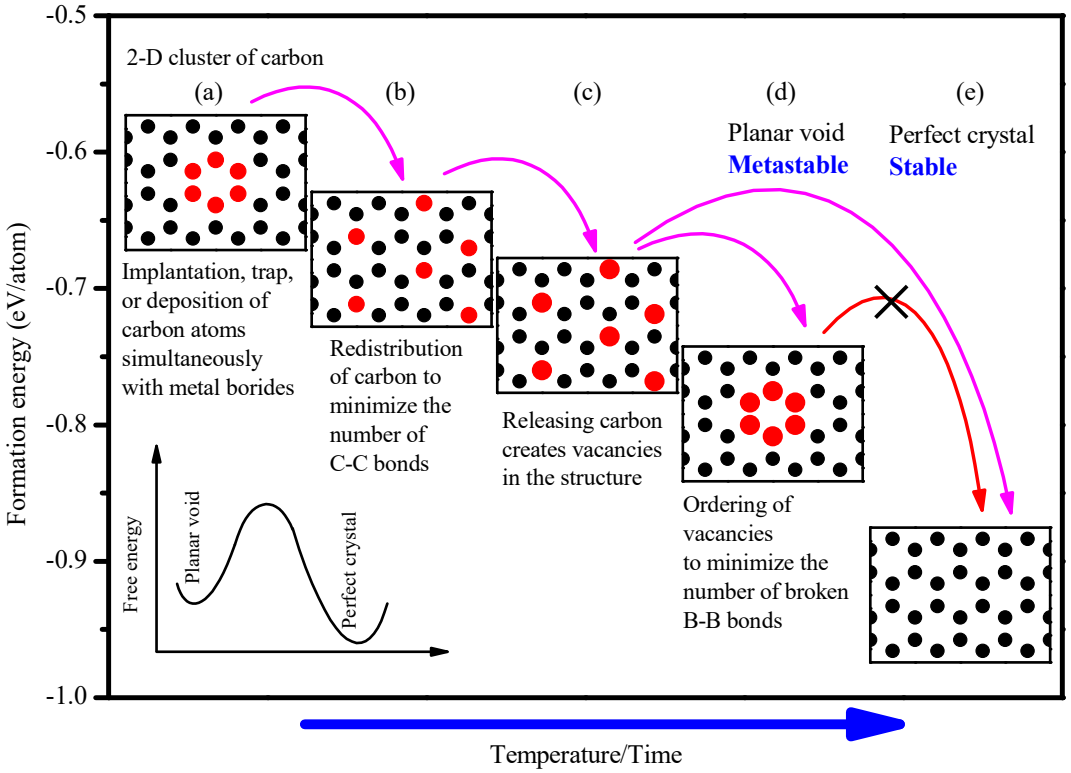


**Figure 2:** Defect transformation as a function of temperature or time towards a (meta)stable arrangement. (a) 2D cluster of carbon atoms at boron sites. (b) Redistribution of C atoms minimising the number of C–C bonds. (c) Carbon atoms tend to leave the structure creating vacancies. (d) Coalescence of vacancies forming a planar void. (e) Perfect crystal obtained by healing the vacancies using B atoms from grain boundaries.

substitutions tend to occur far from each other, minimising the number of formed C–C bonds. Furthermore, vacancies increase the material metallicity, and both types of defects deteriorate the mechanical properties (elastic moduli and predicted hardness).

The findings are summarised in Fig. 2, showing the thermodynamically driven evolution of defect character in the studied class of materials. A trapped carbon cluster is dispersed into individual carbon substitutions which then tend to leave the structure, creating vacancies, and to segregate at grain boundaries. Depending on the presence of a reservoir of boron atoms in the environment, the vacancies either coalesce into a larger planar void or are healed by excess boron, creating a perfect crystal.

## References


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Feng, L., Fahrenholtz, W.G., Hilmas, G.E., Monteverde, F. (2021) Effect of Nb content on the phase composition, densification, microstructure, and mechanical properties of high-entropy boride ceramics. *Journal of the European Ceramic Society,* Volume 41, pp. 92–100.

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