**NdB₆** ceramic nanoparticles: First principles calculations, mechanochemical synthesis and strain engineering

Burçak Boztemur a,b,**, Mubashir Mansoor c,d, Faruk Kaya d, Mantao Huang e, Emre Tekoğlu e, M.Łütfi Öveçoğlu a, Ju Li e, f, Duygu Ağaoğulları a,b,*

a Istanbul Technical University, Faculty of Chemical and Metallurgical Engineering, Department of Metallurgical and Materials Engineering, Particulate Materials Laboratories (PML), Graphene and 2D Materials Laboratory, 34469 Maslak, Istanbul, Türkiye

b Istanbul Technical University, Prof. Dr. Adnan Tekin Materials Science and Production Technologies Applied Research Center (ATARC), 34469 Maslak, Istanbul, Türkiye

c Istanbul Technical University, Faculty of Science and Letters, Department of Applied Physics, 34469 Maslak, Istanbul, Türkiye

d Istanbul Technical University, Faculty of Chemical and Metallurgical Engineering, Department of Metallurgical and Materials Engineering, 34469 Maslak, Istanbul, Türkiye

e Department of Materials Science and Engineering, Massachusetts Institute of Technology, 77 Massachusetts Avenue, Cambridge, MA 02139, United States

f Department of Nuclear Science and Engineering, Massachusetts Institute of Technology, 77 Massachusetts Avenue, Cambridge, MA 02139, United States

**Abstract**

Borides are usually hard and brittle materials; however, we report the synthesis of superplastic nanostructured NdB₆ ceramic powders, counter to the conventional wisdom that borides are always brittle. We investigate that through strain engineering, NdB₆ can be made extremely ductile if the lattice is compressively strained and highly defected, based on transmission electron microscopy (TEM) and density functional theory (DFT) calculations. In this study, the synthesis conditions were designed based on CALPHAD modelling, and the superplastic NdB₆ powders were successfully obtained through mechanochemical synthesis (MCS) of Nd₂O₃, B₂O₃ and Mg initial materials in a high-energy ball mill. Following MCS, the powders were purified in a hydrochloric acid (HCl) containing aqueous solution in order to leach out MgO by-product. The purified powders were characterized using X-ray diffractometry (XRD), Helium (He) gas pycnometry, scanning electron microscopy (SEM) coupled with energy dispersive spectroscopy (EDS), transmission electron microscopy (TEM), particle size analysis (PSA) and magnetometry techniques, which demonstrated...
1. Introduction

Metal borides are important and unique advanced ceramic materials utilized at high-temperature applications. Rare-earth (RE) borides are a family of high-temperature materials with extremely fascinating chemical and structural properties [1,2]. Thanks to the strong bonding of boron, great stability and high hardness in extreme conditions are observed for many boride materials. As a new development, exciting magnetic and electronic properties have been found in the newly discovered RE boron compounds, attributed to their metallic bonding component and contributions of the f-electrons [3,4].

The study of RE borides has attracted a lot of attention over the past three decades. Six distinct families have been discovered, namely: REB2, REB4, RE2B5, REB6, REB12, and REB66 [5]. Amongst the RE borides, RE hexaborides (REB6) have attracted more attention thanks to their extreme characteristics such as low work function, high melting point, chemical stability, magnetic property and superconductivity [6–8]. These properties have also made REB6 of considerable interest as field-emission sources in various devices. REB6 are also used in high-energy optical systems, as sensors for high-resolution radiation detectors and as electrical coatings for resistors because of their low work function, small optical size, high brightness, low volatility at high temperatures, long service life, and the mono energetic character of their thermonic electron emissions [9–11]. Neodymium hexaboride (NdB6) is an important member of REB6 group materials, and has very interesting magnetic and mechanical properties, with one of the lowest work function amongst the REB6 family [7,8]. According to the Nd–B binary phase diagram, Nd2B3, NdB4, NdB6 and NdB66 are the four phases in this binary system, with NdB6 being the most stable high-temperature phase [12]. NdB6 has a cubic structure with a space group of Pm-3m, in which Nd atoms are surrounded by six boron atom octahedra [13]. NdB6 has low density (4.95 g/cm³), high melting point (2610 °C), high thermal conductivity (47 Wm⁻¹K⁻¹) and low thermal expansion coefficient (7.3 × 10⁻⁶ °C⁻¹) [14–18]. NdB6 orders in an A-type collinear antiferromagnetic structure below TN ≈ 8 K [19–22].

Neodymium hexaboride powders can be fabricated by using various synthesis methods. NdB6 has been synthesized by boro/carbothermal synthesis method using carbon and boron carbide, combustion synthesis method, mechanochemical synthesis, flux-controlled self-catalyzed method and facile catalysis-free method [10,14,19,23,24]. For instance, NdB6 nanoparticles with an average particle size of 118 nm belonging paramagnetic behavior at cryogenic temperatures. DFT calculations have been carried out through to investigate the structural, mechanical, electronic, optical, thermodynamic and magnetic properties of NdB6. The impact of various defects was examined, which revealed the significance of boron vacancies and compressive strains in the superplastic form of NdB6.
offers several advantages to the conventional methods of nanoparticle synthesis, namely, the control on purity and particle size, absence of externally applied heat (accepted as room temperature process), versatile experimental set-up, ease of experimental procedure, and strict control over the chemical potentials in the system based on the environmental conditions and precursors that can be utilized [30–32]. This makes it possible to induce a wide range of chemically induced strains (through defect-assisted strain engineering) that ultimately determine the final material properties. Therefore, an experimental study combined with the CALPHAD and DFT modellings is put together for the first time on the superplastic nanostructured NdB$_6$ powders derived from MCS and acid leaching.

2. Experimental and computational methods

2.1. Raw materials and precursor preparation

Nd$_2$O$_3$ (Alfa Aesar, 99% pure), B$_2$O$_3$ (ETI Mine, 98% pure) and Mg powders (Alfa Aesar, 99.8% pure) were used as the starting materials. The average particle sizes of the Nd$_2$O$_3$, B$_2$O$_3$ and Mg initial powders were measured by using a Malvern Mastersizer 2000 particle size analyzer and determined as ~5 μm, 386 μm and 108 μm, respectively. Stoichiometry for the synthesis of NdB$_6$ from the Nd$_2$O$_3$, B$_2$O$_3$ and Mg powders is given by the reduction reaction in Eq. (1). The stoichiometric amounts of the initial reactants were Nd$_2$O$_3$ : B$_2$O$_3$ : Mg = 1.598 : 1.984 : 21 Mg → 2 NdB$_6$ + 21 MgO (1) module was used under 1 atm and non-adiabatic conditions (ΔH ≠ 0) since the experimental set up is not heat insulated, and the temperature of the system can rise up to 600 °C. FactPS and SGTE 2017 databases were selected for the gas, compound and solution phases.

As-blended powders were sealed under Ar (Argon) atmosphere (Linde, 99.999% pure) in an MBraun glove box. For producing NdB$_6$, mechanochemical synthesis (MCS) was triggered by milling of the as-blended powders in a high energy NanoMultiMix mill at 920 rpm for different durations up to 8 h. The required energy needed to initiate the reaction was provided by high energy collisions, induced into powder particles via mechanical deformation. The ball-to-powder weight ratio was fixed at 10:1. Hardened steel vial (50 ml) and hardened steel balls (6 mm diameter) were used as milling media. After MCS, selective acid leaching was applied for the removal of MgO by-product with 2 M, 4 M and 6 M hydrochloric acid (HCl, Merck, 37%) solution under ultrasonic stirring and heating using a Bandelin Sonorex RK-100H ultrasonic bath. The leaching treatment was conducted at 80 °C for 20 min with a solid-to-liquid ratio of 1 g/10 cm$^3$. The residue was then separated from the leaching solution by repeated centrifugation (Hettich Rotofix 32 A, 4000 rpm, 20 min), decantation and rinsing steps. The residue was dried in an FN 500 stove at 80 °C for 18 h in air. The residue is hereafter referred to as leached powders. The schematic of powder synthesis procedure is shown in Fig. 1.

2.3. Characterization

X-ray diffraction (XRD) investigations of the as-blended, mechanochemically synthesized (MCS'd) and leached
powders were performed using a Bruker D8 Advanced Series X-ray powder diffractometer, with CuKα (λ = 0.154 nm, 35 kV and 40 mA) radiation in the 2θ range of 10°–90° incremented at a step size of 0.02° at a rate of 2°/min. The International Center for Diffraction Data® (ICDD) powder diffraction files were utilized to determine the crystal structure and lattice parameter(s) of the crystalline phases. The average crystallite sizes of the MSc-d NdB₆ powders were measured by utilizing Bruker-AXS TOPAS V3.0 software based on the modified Scherrer’s formula [34]. The amounts of the different phases in the MSc-d NdB₆ powders were identified by the semi-quantitative Rietveld refinement method based on the related XRD patterns. The density of the leached powders was measured using Micromeritics AccuPyc II 1340 gas pycnometer in an 1 cm³ sample chamber at room temperature using He gas (Linde, 99.996% pure) as the displacement medium. Particle size analyses (PSA) were conducted for the leached powders using a Microtrac Nano-flex particle size analyzer equipped with a Bandelin Sonopuls ultrasonic homogenizer in alcohol media. Also, surfactants were not used for dispersion in this solution. A Thermo Scientific Quattro S equipment was used for scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) analyses of the MSc-d and leached powders. EDS results were reported as the arithmetic means of three different measurements taken from the same regions in the samples. A JEOL JEM-ARM200CFEG UHR-TEM (equipped with STEM, Cs corrected STEM, EDS, Gatan Quantum GIF and Digital CCD Camera) was used for transmission electron microscopy (TEM) analysis to measure interplanar spacings (d) and particle sizes of the powders. Magnetic measurements were performed using a Quantum Design MPMS3 SQUID (superconducting quantum interference device) magnetometer under an applied field of 200 Oe. UV-VIS spectrum of the synthesized powder was obtained through a Shimadzu UV-260.

2.4. Computational analysis by density functional theory

In order to investigate the lattice parameters, magnetization density, electronic band structures, density of states, thermodynamic functions and elastic properties of the NdB₆ phases, spin-polarized density functional theory (SP-DFT) was applied in this study. The generalized gradient approximation was utilized as the exchange functional, as parametrized by Perdew, Burke and Ernzerhof (GGA-PBE) [35]. Given that the presence of f-electrons can cause significant challenges due to self-interaction error, we have also computed and benchmarked the lattice parameters and the magnetic properties using hybrid density functional theory, with HSE06 [36] as the exchange functional, which shows consistent results. A planewave cut-off energy of 500 eV was used, with a Gaussian integration scheme and a smearing width of 0.05 eV. A minimum k-point spacing of 0.2 Å⁻¹ was applied. During the MCS and its subsequent leaching, there are possibilities for the introduction of intrinsic defects (such as Nd or B vacancies) and/or doping with Mg, H, Cl and O. Therefore, to better understand the changes induced by such defects, their formation energies and magnetic moments have been calculated by using the supercell approach to minimize spurious defect-defect interactions. In order to investigate the d-spacing changes that will be induced by these defects, several supercells are constructed from the primitive structure to 2 × 2 × 2, 3 × 3 × 3 and 4 × 4 × 4 supercells, where dopants are positioned in substitutional (Mg, Cl, O) or interstitial (H) sites. The defect formation energy (ΔHᶠˢᵉᵗ) is calculated as proposed by Zhang and Northrup in Eq. (2) [37].

$$\Delta H^{\text{f}\text{S}^e} = E^{\text{tot}} - \sum n_i \mu_i + \frac{q}{2}(E_f + E_{\text{VM}}) + \frac{1}{2} \sum q_i (\frac{1}{2} \sum_{i,j} \sigma_{ij} E_{\text{ij}})$$

(2)

$$E^{\text{tot}}$$ is the total energy difference of the defective and pristine supercells. $$E_f$$ is the equilibrium Fermi energy and $$E_{\text{VM}}$$ is the valence band maximum, with q being the defect charge. $$E_{\text{NV}}$$ is the FNV correction [38] due to charged defects. Given the overlap of the valence and conduction bands in these structures, charged defects are not considered, because such defects cannot exist under these circumstances [39], hence, q = 0 at all times. Therefore, the defect formation energies are directly linked to the chemical potential of their constituent elements ($$\mu_i$$), as elaborated upon in detail by Freysoldt et al. [40].

The phonon density of states, and consequently the thermodynamic functions (heat capacity, vibrational entropy and enthalpy) were calculated based on the approach proposed by Parlinski, Li and Kawazoe [41]. The elastic constants were calculated by considering strained cells [42,43]. The total energy difference of each strained cell when compared to pristine cell was used, as shown in Eq. (3), based on applied engineering strain e. , and changes in ductility are also calculated similar to the methodology applied by Tan et al. [44].

$$\Delta E^{\text{tot}}_{\text{strain}} - \Delta E^{\text{tot}}_{\text{pristine}} = \frac{1}{2} \sum_{i=1}^{8} \sum_{j=1}^{8} C_{ij} e_i e_j$$

(3)

Here $$V_e$$ is the initial volume of the cell. The Poisson’s ratio, shear ($$G$$), bulk ($$B$$), longitudinal ($$\rho$$) and Young’s ($$Y$$) moduli were calculated based on the fundamental principles of elasticity (Voigt-Reuss-Hill model) [45]. The impact of strain on the magnetic moment was analyzed by performing a DOS calculation on the strained cells. For estimating the nano-indentation Vickers hardness values, the empirical model of Chen et al. [46] was applied. Similarly, based on the elastic constants, the thermal expansion coefficient as a function of temperature was calculated through the Grüneisen-Debye approximation [47]. Non-stoichiometry and associated strains are known to cause significant changes in material behavior [48]. Therefore, the elastic properties were also calculated in the case of applying hydrostatic strain on the cell in order to estimate the impact of various strains on the mechanical properties, optical and magnetic properties.

An important property of the hexaboride structures is their work function ($$\Phi$$) [49,50], which has been calculated for the (100) and (111) planes, by considering the changes in the local electron potential across a slab, and the difference in the bulk electron potential when compared to the vacuum level, as shown in Eq. (4) for plane i. The suitability of this approach was recently discussed by Jiang et al. [51].

$$\Phi_i = V^{\text{vac}}_i - E_f$$

(4)
For this purpose, seven consecutive cells were considered in a $1 \times 1 \times 7$ supercell, with $10\text{Å}$ of vacuum between periodic slab images.

In order to estimate the color of synthesized powders under various conditions, we have applied the methodology of Gajdoš et al. [52] for the calculation of the imaginary ($\epsilon'$) and real ($\epsilon''$) parts of the dielectric function, as a function of photon frequency $\omega$. The real component of the dielectric tensor was then calculated through Kramers-Kroning transformation as shown in Eq. (5). $P$ being the principal value, and $\eta$ is the complex shift taken as 0.1.

$$\epsilon'(\omega) = 1 + \left( \frac{2P}{\pi} \right) \int_{0}^{\infty} \frac{\epsilon(\omega) \omega}{\omega^2 - \omega^2 + i\eta} d\omega$$

(5)

The frequency-dependent absorption coefficient ($\Delta$) is then calculated using Eq. (6) [53], where $c$ is the speed of light in vacuum. The Bouguer-Lambert’s law is applied for obtaining the transmission spectra $T(\omega)$ in Eq. (7), with the path length $L$ based on the synthesized particle size.

$$\Delta(\omega) = \sqrt{\frac{2\omega}{c}} \sqrt{\epsilon''^2 + \epsilon'^2 - \epsilon''^2}$$

(6)

$$T(\omega) = e^{-\Delta L(\omega)}$$

(7)

The respective Red Green Blue (RGB) color coordinates were found based on the D65 illumination standard, through the conversion of the transmission spectra into XYZ tristimulus values, which were then transformed into RGB values as follows. These calculations were done as in Eq. (8) and Eq. (9).

$$[r \ g \ b] = 255 \begin{bmatrix} 3.240 & -1.537 & -0.491 \\ -0.969 & 1.876 & 0.042 \\ 0.056 & -0.204 & 1.057 \end{bmatrix} [X \ Y \ Z]$$

(8)

$$[R \ G \ B] = \begin{bmatrix} \frac{r}{2} \\ \frac{g}{3} \\ \frac{b}{2} \end{bmatrix}$$

(9)

3. Results and discussions

We have demonstrated the production of superplastic NdB$_6$ nanostructured powders through the versatile method of MCS via high energy ball milling, which is a simple and room temperature process that also enables the control of product microstructure (phase, shape, size, etc.), and widely used to produce homogeneous materials [30–32,54]. This method can fulfill the requirements for producing superplastic nanostructured NdB$_6$. The reason for the superplasticity is rooted in the extreme compressive stress that becomes possible through the high energy ball milling. The sequence of the production process highly favors formation of boron vacancies that are crucial for superplasticity. We observe changes in the color and reduced magnetic moment of the NdB$_6$ due to this production process, the reasons for which are explained through an atomistic perspective in the following sections.

### Table 1 – Properties of the NdB$_6$ phase as predicted by DFT.

<table>
<thead>
<tr>
<th>Property</th>
<th>Pristine NdB$_6$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lattice parameters (Å)</td>
<td>$a = 4.134$</td>
</tr>
<tr>
<td>Space group</td>
<td>Pm-3n</td>
</tr>
<tr>
<td>Bulk density ($g/cm^3$)</td>
<td>4.914</td>
</tr>
<tr>
<td>Zero point energy, ZPE (eV)</td>
<td>0.438</td>
</tr>
<tr>
<td>Work function, $\Phi$ at 0 K (eV)</td>
<td>3.37 (100)</td>
</tr>
<tr>
<td>Magnetic moment ($\mu_B$)</td>
<td>3.195</td>
</tr>
<tr>
<td>Elastic constants (GPa)</td>
<td></td>
</tr>
<tr>
<td>$C_{11}$</td>
<td>468.33 ± 3.42</td>
</tr>
<tr>
<td>$C_{12}$</td>
<td>27.12 ± 3.42</td>
</tr>
<tr>
<td>$C_{44}$</td>
<td>65.78 ± 4.83</td>
</tr>
<tr>
<td>Bulk modulus (GPa)</td>
<td>174.19</td>
</tr>
<tr>
<td>Shear modulus (GPa)</td>
<td>109.58</td>
</tr>
<tr>
<td>Young’s modulus (GPa)</td>
<td>270.70</td>
</tr>
<tr>
<td>Poisson’s ratio</td>
<td>0.240</td>
</tr>
<tr>
<td>Pugh’s ratio</td>
<td>1.590</td>
</tr>
<tr>
<td>Vickers hardness (GPa)</td>
<td>15.15</td>
</tr>
<tr>
<td>Thermal expansion (°C/K)</td>
<td>8.662 (at 298 K)</td>
</tr>
<tr>
<td></td>
<td>11.124 (at 1000 K)</td>
</tr>
<tr>
<td>Grüneisen parameter</td>
<td>1.453</td>
</tr>
<tr>
<td>Debye temperature (K)</td>
<td>721.30</td>
</tr>
<tr>
<td>Color</td>
<td>Purple</td>
</tr>
</tbody>
</table>
as 2834 °C with the increasing B₂O₃ content, which shows the extremely exothermic nature of this reaction. The ΔH and ΔG values were calculated to be −3904.9 kJ/mol and −3751.3 kJ/mol at 25 °C, respectively. Fig. 3a elucidates the equilibrium reaction products as a function of temperature. Given the non-adiabatic nature of the experimental set-up, which is known to reach a temperature of approximately 600 °C, varying B₂O₃ contents were also considered (Fig. 3b). It is noteworthy that higher synthesis temperatures are found to cause gasification of precursors such as B₂O₃ and Mg, which should be avoided. Fig. 3b demonstrates the simulated reaction product stoichiometries (Eq. (1), A = 6 mol) at varying temperatures under 1 atm atmospheric pressure. It was found that between 25 °C and 400 °C, two boride phases form, mainly NdB₄ together with Mg(B₆)₂. Also, the reduction product MgO forms, with minor quantities of Mg₃B₂O₆ as well as retained

Fig. 2 – Schematic of the atomic arrangements of pristine NdB₆ (a). The blue atoms show Nd, and lime color atoms represent B, as well as the DOS (b) and thermodynamic properties of NdB₆ (c,d).

Fig. 3 – Thermochemical simulation of the reaction products for the stoichiometric powder blend (a), the effect of varying B₂O₃ content at a fixed temperature of 600 °C (b), dashed line corresponds to the stoichiometric powder blend.
excess B$_2$O$_5$. This suggests that the complete reduction of B$_2$O$_3$ phase may not be achieved at low temperature range. Above this critical temperature (400 °C), the aimed NdB$_6$ phase is obtained as the sole product of the reaction, if the B$_2$O$_3$ content is well controlled. The CALPHAD model shows the thermodynamic possibility of achieving NdB$_6$ under the experimental set-up used, which can be purified through leaching in HCl solution for dissolving the MgO by-product.

The use of HCl acid during leaching and the significant formation of Mg-related phases during the production process warrant a study on the changes in the lattice by doping H, Cl, Mg or O. The defect formation energies for some of the possibilities that seem likely are listed in Table 2. The calculations illustrate that it is rather unlikely for Mg atoms to occupy Nd sites, given the reference chemical potentials considered for the experimental set-up used. Placement of Mg as anti-site defect (taking over B sites) is more likely, although the defect formation energy is extremely high, and makes such defects rather inconsequential, given the Arrhenius relationship for defect formation energy ball mill under the framework of MCS for this study.

The calculations also show that the defect formation energies of Cl and O that occupy a B site are negative, which can facilitate the desired compressive strains through inducing B-vacancies.

These references are based on the abundance of O$_2$ gas, and HCl during MCS and leaching, as well as the compatible phases that have been calculated by FactSage. It should be noted that $\Delta H_f^*$ values of Table 2 are formation energies that are based on chemical potentials given in Eq. (11) to Eq. (16). However, the $\Delta H_f$ column that keeps the chemical potentials as variables can be used for any other experimental condition. The calculations demonstrate that the most likely simple point defects that may occur are V$_B$ (B vacancy), Cl$_B$ (Cl positioned in B site), O$_B$ (O positioned in B site), and V$_B$ + H$_i$ (B vacancy filled with H interstitial). A schematic representation of the defect structures is shown in Fig. 4. As explained above, to achieve our aim for synthesizing a ductile boride, the formation of B vacancy is crucial, and the production process designed here allows such defects to form, which would be otherwise challenging when considering the stability of borides and their strong covalently bonded structures.

The theoretical predictions of Pan et al. [29] show an increasing Pugh’s ratio (ratio of bulk to shear modulus) as boron vacancy concentration increases in ReB$_2$. This was attributed to reduced lattice parameters that lead to weak hybridization between metal cation and boron. However, they have also predicted difficulties in creating such defects. Therefore, by using a high energy ball mill during MCS, instead of a low speed mill such as planetary ball mill, it is possible to forcefully reduce the lattice parameters by compressively straining the unit cells. Hence, we chose high energy ball mill under the framework of MCS for this study, which can facilitate the desired compressive strains through inducing B-vacancies.
The MCS method is known to induce residual lattice strains and a plethora of studies on this topic have elucidated the inevitability of strain induced structures through either mechanical or defect induced means [55]. MCS provides an excellent flexibility on the chemical potential equilibria, simply based on the precursors and environment that are used during synthesis (see Eq. (11) to Eq. (16)). Given the prevalence of B-vacancy in the structure as per our DFT calculations (Table 2), and the eventual appearance of compressive strains due to B-vacancies that were also validated experimentally (shown in the following sections through TEM investigations), we estimated the changes in the elastic constants due to various local strains through DFT. The prevalence of strain dependent materials properties is a widely studied phenomenon, and it is known that strains at the atomic level can significantly alter mechanical, optoelectronic and even catalytic properties [48,56]. It is noteworthy that chemically induced strains (through defects) are not necessarily an intrinsic outcome of the MCS production method [38,54], but rather an effect of the chemical potential equilibria that emerges during synthesis. Therefore, this study demonstrates that it is possible to use the MCS along with certain precursors and environmental conditions that yield chemical potentials of interest for facilitating defects of interest. Thus, inducing strains that are otherwise not possible, make MCS a viable method for strain engineering. We conducted the DFT calculations based on relaxing cell parameters under hydrostatic stresses. It is found that NdB₆ shows superplasticity if the cell is compressively strained such that the lattice is under compressive stresses beyond 15 GPa (as shown in Fig. 5a). The main reason for this phenomenon is the change in C₄₄ as a function of applied stress, which approaches zero under extreme compression. This is a sign of superplasticity as proposed by Saito et al. [57] and Souvatzi et al. [58]. In fact, the main reason is diminishing critical shear stress, which approaches zero as C₄₄ approaches zero. Therefore, through the application of MCS using high energy ball mill, we have theoretically predicted that it is possible to synthesize superplastic NdB₆, if the lattice is sufficiently compressed, either by external stress or chemical doping or defects. This is also verified by considering the variations in the Pugh’s ratio [59] (Fig. 5b), which shows compressive strains cause a transition from brittle to ductile behavior.

### 3.3. Phase analysis of synthesized powders

The XRD patterns of the as-blended Nd₂O₃–B₂O₃–Mg powders, and those MCS d for different durations up to 4 h are shown in Fig. 6a. In the XRD pattern of the as-blended (non-milled) powders, Nd₂O₃ (ICDD Card No: 00-043-1023, Bravais...
lattice: primitive hexagonal, \(a = 0.382\) nm and \(c = 0.599\) nm), Mg (ICDD Card No: 00-004-0770, Bravais lattice: primitive hexagonal, \(a = 0.321\) nm and \(c = 0.521\) nm) and Nd(OH)\(_3\) (ICDD Card No: 01-083-2035, Bravais lattice: primitive hexagonal, \(a = 0.329\) nm and \(c = 0.521\) nm) phases were detected, as expected. The characteristic peaks of B\(_2\)O\(_3\) were not observed in the XRD pattern of the as-blended powders because of its amorphous nature. The intensities of the Nd\(_2\)O\(_3\) and Mg phases decreased with increasing milling time. This indicates a reduction in the average crystallite sizes of the Nd\(_2\)O\(_3\) and Mg powders, and hence an increase in their reactivity for the forthcoming reduction reaction. Also, Nd(OH)\(_3\) phase is no longer observed as the milling time increases. As seen from Fig. 6a, the powders milled for 1 h contain Nd\(_2\)O\(_3\), MgO (ICDD Card No: 01-079-0612, Bravais lattice: face centered cubic, \(a = 0.422\) nm), NdB\(_6\) (ICDD Card No: 03-065-1828, Bravais lattice: primitive cubic, \(a = 0.413\) nm) and NdB\(_4\) (ICDD Card No: 00-024-1458, Bravais lattice: tetragonal, \(a = 0.722\) nm and \(c = 0.410\) nm) phases. Besides, the intensity of MgO phase is higher for the 1 h milled powders compared to those of other

Fig. 5 – Variations in \(C_{44}\) as a function of hydrostatic stress (a). The negative stresses are tensile, and the positive values are compressive. Superplasticity is inevitable as \(C_{44}\) approaches zero, which is further supported by the changes in the Pugh’s ratio (bulk to shear modulus ratio), which demonstrates a transition from brittle to ductile behavior under compressive strains as well (b).
Fig. 6 - XRD patterns of the (a) as-blended Nd$_2$O$_3$-B$_2$O$_3$-Mg powders and those mechanochemically synthesized for 1 h, 2 h, 3 h and 4 h and (b) 5 h, 6 h, 7 h and 8 h, (c) Average crystallite sizes of NdB$_6$ phase in the mechanochemically synthesized powders versus milling duration plots, and corresponding Rietveld analyses showing the NdB$_6$, NdB$_4$ and MgO phase weight percentages.
milling times. After 1 h, the intensity of MgO phase became more stable and comparable with each other. Therefore, 1 h milling duration can be considered as the initial point for the formation of the boride phases. At the end of 3 h milling, the only detected phases were mostly NdB₆ and MgO along with minor amounts of NdB₄ (Fig. 6a). XRD pattern of the 5 and 8 h milled powders are illustrated in Fig. 6b, showing that extended milling duration did not change the nature of the resulting products, as NdB₆ and MgO phases are still present with NdB₄ phase, and no new phases have formed. Besides, the peak intensities of the NdB₆ and MgO phases gradually decreased from 5 to 8 h milling as seen from Fig. 6b, that may be attributed to the crystallite size reduction due to the high and repeated impact energy acquired during milling. Although the NdB₆ phase formation starting from different raw materials was previously reported in the literature [13,23,24,27], the occurrence of NdB₄ with NdB₆ is being reported for the first time. The reason for the observed phase transformations is well-explained through the thermochemical CALPHAD calculation through FactSage. The average crystallite sizes and phase analyses of the powders milled for different durations are shown in Fig. 6c. The most intense five peaks (diffracted from (100), (110), (111), (200) and (210) planes) were selected for the TOPAS measurements. On the basis of the related XRD patterns, the average crystallite sizes of the NdB₆ phase in the powders milled for 2–8 h were calculated as 92.6, 91.86, 89.08, 85.52, 83.32, 80.62 and 76.68 nm, respectively. Also, after 5 h of milling time, the amounts of NdB₆, NdB₄ and MgO phases no longer show significant changes based on the Rietveld analyses. Therefore, 5 h was chosen as the optimum milling time.

In order to dissolve the unwanted reaction product (MgO), leaching was done. Different molarities of HCl acid were also tried for leaching. XRD results are given in Fig. 7. MgO phase

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**Fig. 7** – XRD patterns of the NdB₆ powders after 2 M, 4 M and 6 M HCl leaching. This powder is originated from Nd₂O₃–B₂O₃–Mg blends mechanochemically synthesized for 5 h.
was observed in the 2 M leached powders. However, impurities were no longer observed in the 4 M leached powders. Therefore, 4 M HCl acid solution was chosen for further leaching treatments. As clearly seen in the XRD pattern of the NdB₆ powders that are MCS'd for 5 h and leached with 4 M HCl, the acid concentration is sufficient to remove the MgO phase completely from the powders. On the other hand, no impurity phases were observed in the XRD pattern within the detection limit of the used diffractometer (<2 wt %). Moreover, based on the XRD pattern, the average crystal size of the 4 M leached powders was determined as 117.3 nm.

Fig. 8 – SEM image of the NdB₆ powders under 13,000× magnifications (a) and the particle size distribution (b) followed by SEM images under magnifications of 50,000× (c), 100,000× (d) and TEM images for NdB₆ leached with 6 M HCl acid (e–h).
Upon comparing the results of this study with the published literature, it is seen that NdB₆ phases are produced only through demanding procedures that require high temperature (1500 °C for 4 h holding time) [13], or application of pressure (20 MPa) through combustion synthesis [23]. Similarly, boron-rich RE boride, NdB₆ was synthesized at 1600 °C and 4.0 GPa pressure at a duration of 1.5 min [27]. These methods require considerable time and energy to reach the synthesis temperature and to complete the reactions, hence from the perspective of green and eco-friendly technologies, the production of NdB₆ is significantly more advantageous through the method proposed here, which may be further extended into other rare earth hexaborides through future research. Moreover, any process that requires high temperatures will anneal the strains, and thus a superplastic NdB₆ (as shown in Fig. 5) cannot become possible.

### Table 3 – The variations in d-spacings due to the defects that are probable based on DFT and measured EDS values.

<table>
<thead>
<tr>
<th>Structures</th>
<th>Planes</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>d (100) (Å)</td>
<td>d (110) (Å)</td>
<td>d (111) (Å)</td>
<td></td>
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<tr>
<td>Pristine NdB₆</td>
<td>4.143</td>
<td>2.929</td>
<td>2.392</td>
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<tr>
<td>0.62% B-Vacancy</td>
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<td>2.931</td>
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<tr>
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<tr>
<td>0.53 at % O</td>
<td>4.141</td>
<td>2.928</td>
<td>2.398</td>
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</table>

Fig. 8 shows SEM images with different magnifications (13,000, 50,000 and 100,000 ×). Particle shape was seen in mixed

3.4. **SEM, TEM and lattice compression observations**

Fig. 9 shows TEM images for NdB₆ leached with 6 M HCl acid, as correlated with DFT calculated interplanar spacings for (100), (110) and (111) planes under various lattice stresses.
morphology according to the SEM images. The general EDS analysis taken from the area in Fig. 8c reveals the amounts of Nd, B, O, Mg and Cl elements as 24.95, 72.39, 2.4, 0.18 and 0.08 at %, respectively. This shows significant B vacancy as the pristine structure must contain ~86 at % B. In addition, the PSA graph as given in Fig. 8b illustrates that the average particle size of the NdB₆ was about 118.9 nm which is in the similar range observed in the SEM image in Fig. 8c. Lognormal distribution type was observed for this graph. Higher magnification of SEM image (Fig. 8d) for NdB₆ shows particle size between 80 and 120 nm. Also, the tap density of NdB₆ powders was measured as 4.03 ± 0.01 g/cm³. This rather large particle size (Fig. 8d) and quite dense interior (4.03/4.95 = 81.4%) indicate the malleability of the NdB₆ produced, which must undergo cold welding at room-temperature. TEM images are given in Fig. 8e–h, with the average particle sizes found to be smaller than 200 nm. Also, particle shape is once again seen to be in various mixed morphologies. Considering the EDS and defect formation energies, we have also analyzed the changes in d-spacing that should be expected based on a full geometry relaxation through DFT, as shown in Table 3. It is clear that boron vacancy causes significant contraction in d-spacing.

TEM offers the opportunity to measure interplanar spacings experimentally. Multiple samplings were made from different areas. For each area, a minimum of five measurements were done, and the results are given in Fig. 9. For (100), (110) and (111) planes, the interplanar spacings given in crystallographic databases, and PDF-cards are 4.128, 2.919 and 2.383 Å, respectively [60]. However, these values do not match with our experimental measurements, and the synthesized nano-powders show significantly smaller interplanar spacing, demonstrating the compressive strain, as anticipated. The changes in interplanar spacing as a function of stress were calculated using DFT, and the results are shown in Fig. 9. Bringing together the TEM interplanar spacing data and DFT prediction of spacing changes due to stress, shows that the

Fig. 10 – Experimental magnetic moment analysis for NdB₆ leached with 6 M HCl acid (a), explained through changes in DOS due to stress as calculated by DFT (b,c), experimentally obtained UV-VIS spectra, with an inset photograph of the synthesized powders, and DFT computed changes in color as a function of stress are shown (d).
synthesized material is under compressive stresses of more than 20 GPa, which coincides with the threshold for superplasticity.

3.5. Magnetic and elastic properties, and color variations due to lattice strains

The magnetic moment of NdB₆ was experimentally measured by Stankiewicz et al. [7] as 3.15 μ₀/f.u., which is in good agreement with our DFT computed value of 3.195 μ₀/f.u. For the pristine cell, further validating the computational methodology used in this study. However, the experimentally measured magnetic moment of the NdB₆ synthesized in this study is lower by orders of magnitude as seen in Fig. 10a. This radical decrease is explained when considering the changes in the DOS due to strain. Although boron vacancies and hydrogen interstitials can reduce the magnetic moment as well (Table 2), the fundamental cause is attributed to the changes induced in lattice parameters due to the defects. For a lattice under tensile strain (Fig. 10b), a rise in the magnetic moment is inevitable, however, for compressive strain, a steep fall in magnetic moment is seen. The spin channels become highly symmetric as compressive strain increases, causing a fall in the magnetic moment. Given that the main cause of this fall in the magnetic moment is compressive strain, it is possible to recover the magnetic property through annealing treatments, preferably at high temperatures. Color is another interesting change that is seen in the synthesized powders. Pristine NdB₆ is known for its purple color, which was also successfully predicted by the computational methodology used in our study. However, as the lattice goes through compressive strains, the red component of the RGB color coordinates is reduced, and the color shifts to a vivid blue, as predicted by the DFT calculations shown in Table 4. This is in direct agreement with our experimental observations, as the color of the synthesized powder is vivid blue as well.

4. Conclusions

In the present study, superplastic nanostructured NdB₆ ceramic powders were successfully prepared through a simple two-step process that includes mechanochemical synthesis via high energy ball mill, followed by purification through HCl leaching. The results of this study can be summarized as follows.

- A novel and simple process for synthesizing superplastic nanostructured NdB₆ ceramic powders was achieved by...
mechanochemical reaction of powder blends containing stoichiometric amounts of Nd2O3, B2O3 and Mg powders.

- During the mechanochemical processing of Nd2O3, B2O3 and Mg starting powders, the formation of the NdB6 phase started only after 1 h of milling. Extending the milling duration to 5 h resulted in the major NdB6 and MgO phases in addition to the minor NdB4 phase, as predicted by the CALPHAD calculations.

- Powders milled for 5 h were successfully purified by leaching in 6 M HCl resulting in the formation of high-purity NdB6 powders with mixed rounded-shape morphology (average size of 118.9 nm) free from undesired MgO.

- According to the DFT calculations, formation of boron vacancy is highly favorable under the applied mechanochemical synthesis conditions, which causes compressive strains in the NdB6 lattice.

- It is found that the NdB6 becomes superplastic as C44 approaches zero under the chemically induced compressive lattice stresses of more than 15 GPa, followed by a significant reduction in hardness and increase in the Young's modulus.

- The magnetic moment of the synthesized powder is seen to be orders of magnitude lower than that of the pristine NdB6. This annihilation of the magnetic moment is explained through the density of states (DOS) calculations on the compressively strained NdB6 lattice, which demonstrate a similar reduction trend in the magnetic moments.

- The color of pristine NdB6 is known to be purple, however, the color of the synthesized powders is blue. The DFT calculations on the dielectric function show a transition from purple to blue under compressive lattice stresses of more than 10 GPa, verifying the experimental observations.

Author contributions

B.B. performed formal analysis, investigations, writing-original draft preparation. M.M. performed DFT investigations, conceptualization, writing-original draft preparation. F.K. investigated FactSage and performed formal analysis. E.T. performed analysis. M.H. performed magnetic analysis. M.L.O. performed reviewing and editing. J.L. performed conceptualization, reviewing and editing. D.A. supervised, performed project administration, conceptualization, writing-original draft preparation.

Notes

The authors declare no competing financial interest.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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References